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IV.—NOTES ON THE SODA-LIME METHOD FOR DETERMINING NITROGEN.

BY W. O. ATWATER AND C. D. WOODS.

A series of studies of the chemistry of animal tissues, especially of fish, in this laboratory, have involved a large number of nitrogen determinations for which the soda-lime method had been employed. The importance of securing results as nearly accurate as practicable has led to a number of observations regarding the methods of manipulation and the sources of error and ways of avoiding them. The accuracy of the soda-lime method has been called in question, and there are still wide divergences of opinion regarding some of the details, despite the pains that have been taken to investigate them. Partly because our experience has convinced us that when rightly manipulated it gives excellent results, and partly because of the propriety of describing the methods followed in the studies referred to, in connection with an account of them to appear in these pages, the following statements seem not out of place. We shall speak first of some points regarding reagents, apparatus, and manipulation.

Soda-lime.

Preparation.—Instead of buying soda-lime at the ordinary price, we have found it very easy and far more economical to make it in the following way, which we believe is practised elsewhere:

One kilogram of commercial caustic soda is dissolved in hot water and the solution poured upon 2.5 kilos of pulverised quick-lime in an iron kettle, care being taken to have enough water in the solution to ensure the slaking of the lime. The kettle is put over a hot fire and the contents are well stirred until the excess of water is removed and the mass is fused. It is ground while warm and kept in tightly stoppered bottles (caoutchouc stoppers have not, in our experience, sufficed to keep out the moisture on long standing) until used. Enough for several hundred nitrogen determinations is thus easily made in a very short time and at a cost for materials scarcely worth mentioning.

The use of an iron or Hessian crucible, as commonly recommended,[1] for fusing the soda-lime we find entirely unnecessary. The precaution that the soda-lime should not contain enough of carbonates to effervesce strongly on application of acid[1] is, of course, needless when this way of making is followed, and would seem, from the results obtained with Johnson's soda-lime (see beyond), to be entirely uncalled for.[1]

We have found it convenient to divide the ground material into a finer portion with which the substance containing the nitrogen to be determined is mixed, and a coarser portion to be used for the anterior layer in charging the combustion tubes. That which passes through a sieve with meshes of $\frac{3}{4}$ mm. works very well for the finer, and that which, not passing this sieve, passes one of 2 mm. is satisfactory for the coarser portion. An ordinary drug mill, which costs but little and is useful for other purposes, serves well for the grinding.

Effect of varying proportions of soda and lime.—The following figures from our laboratory note-books are perhaps worth recording. The determinations were made with specimens of soda-lime in which 1.75, 2, and 2.5 parts by weight of quick-lime were used for each part of caustic soda. The mixtures are computed to contain from 22 to 16 per cent. of sodium oxide. The percentages of nitrogen are calculated on water-free substance.

[1] Vid. Neues Handwörterbuch der Chemie **1**, 482, and Fresenius' Quant. Analysis.

TABLE I.

In Flesh of	Percentages of Nitrogen obtained.	
	Soda : lime :: 1 : 1.75	Soda : lime :: 1 : 2
Lobster, . . .	13.10	13.09
Mullet, ...	12.44	12.47
Yellow Perch, .	14.52	14.55
Sheep, ...	6.97	6.96
"	3.58	3.59
	Soda : lime :: 1 : 1.75	Soda : lime :: 1 : 2.5
Sheep, ...	5.56	5.59
"	5.98	6.02
"	7.36	7.38
"	4.67	4.71
"	4.65	4.62

The above determinations, which, it will be observed, were made in flesh with varying quantities of fat, from that of fish containing only a fraction of one per cent. to that of sheep (mutton) in which the fat very largely exceeds the protein, show no disagreement of duplicates exceeding 0.04 per cent., and imply that the quantity of nitrogen obtained is the same whether the larger or the smaller proportion of lime is used. The soda-lime with 1¾ part of lime to one of soda was very fusible. That with 2½ of lime to one of soda was reasonably hard, and was used in nearly all of the determinations hereafter reported. For a time we were inclined to like the more fusible mixture, since in the combustion it distributed itself over the inner surface of the tube, leaving in the anterior portion a channel, through which the gases formed in the combustion must pass. For reasons to be given later, it is our belief that one source of error in the soda-lime method is the incomplete ammonification of the nitrogenous compounds formed by the destructive distillation, and that to obviate this difficulty it is well for the gases to pass over a large surface of hot soda-lime. The formation of this tubular channel in the anterior portion of the combustion tube seemed especially favorable for bringing the gases into contact with the soda-lime, but the very fusible soda-lime is in some respects inconvenient, and after a time we came back to the use of the comparatively infusible mixture of one part of caustic soda to 2½

of lime, depending upon the coarse particles in the anterior layer of soda-lime for the needed surface.

Ordinary vs. Johnson's soda-lime.—The mixture of sodium carbonate and slaked lime recommended by Johnson[1] has proved very satisfactory, being easily and cheaply made, and, so far as we have observed, giving the same results as the common soda-lime, as shown in Table II.

TABLE II.

In Flesh of	Percentages of Nitrogen found with	
	Ordinary Soda-lime.	Johnson's Soda-lime.
Halibut, ...	6.03	6.04
Herring, ...	7.04	7.01
Salmon, ...	8.76	8.75
"	9.89	9.84
Shad, ...	9.92	9.87
Porgy, ...	10.78	10.75
Mackerel, ...	11.26	11.23
Trout, ...	13.25	13.24
Flounder, ...	14.11	14.09

The figures obtained with the two kinds of soda-lime are practically identical, thus agreeing with those obtained by Johnson and Jenkins.[2]

We might add that in determinations of nitrogen in vegetable material (peas) by Mr. Haynes, a student in this laboratory, slaked lime as recommended by Johnson[3] gave the same results as soda-lime. These and other observations, which it will perhaps be superfluous to cite in detail, seem to imply that neither the presence of carbonic acid in the soda-lime nor the proportions of lime and soda, at least within the limits which obtained in the above cases, have any appreciable effect upon the amount of nitrogen obtained from the nitrogenous compounds of flesh. The practical identity of the results obtained with these different reagents accords entirely with the idea which has been brought prominently forward of late, that the ammonifying agent is superheated steam.[4]

Testing the purity of soda-lime by sugar and other reagents.—In testing the purity of soda-lime by combustion with sugar, as

[1] This Journal **1**, 77. [2] Loc. cit. [3] This Journal **6**, 61.
[4] Vid. Grouven, Landw. Vers. Stationen **28**, 343, and Johnson, loc. cit.

is sometimes recommended, we have occasionally met with very perplexing results. At times we have found apparent indications of nitrogen, while at other times, with the same materials, more alkali was required to neutralise the acid after than before the combustion, which implied that acid products had been formed from the sugar. To obtain some definite data on this matter the determinations in Table III were made. To insure correctness in measurements of the standard solutions, extremely narrow burettes, graduated to fiftieths of a cc., were employed, and especial pains were taken, by cleaning the burettes and working at ordinary temperature, to make the titrations accurate.[1] One cc. of standard acid was used in each case. The quantities of solution to be titrated were thus so small that with cochineal solution very accurate titration was possible. The sugar employed was that commonly sold in large crystals as "rock candy," and was recrystallised from alcohol to insure greater purity. One cc. of standard acid corresponded to, approximately, 10 mgm. of nitrogen. At each titration of acid used for the combustion a cubic centimeter of fresh acid was compared with the alkali. The results of the two titrations are placed opposite each other in the table. Tests made at the same time with oxalic acid and stearin are given with those of the sugar. By medium heat is to be understood a temperature high enough to make the combustion tube slightly red and give a tinge of the familiar yellow color to the soda-lime; by high heat, a heat as great as the tubes, of the most difficultly fusible Bohemian glass we could obtain, would endure without bursting, the quantity of acid in the bulb tube being made very small so as to reduce the pressure to a minimum. The agreement of titrations in the combustions of stearin and oxalic acid implied that the latter, as well as the soda-lime, were free from nitrogen and yielded no acid products. The differences in the amounts of standard alkali required for neutralisation after the combustions with sugar, though absolutely small, were evidently much outside the limits of error, and are most easily explained by the assumption that the sugar contained a minute trace of nitrogen, which appeared as ammonia in the first of the two cases where the combustion was carried on at medium heat, and was more than neutralised by the acid products formed at high heat. The difference between the results with sugar at medium heat and those with

[1] See article on "Burettes and Pipettes" in Journal of Analytical Chemistry, Vol. 1, Part 4.

stearin and oxalic acid was about 0.12 cc. of alkali, which would be equivalent to some 0.3 mgm. of nitrogen. This would imply 0.07 per cent. of nitrogen in the sugar. The determinations at high heat implied an amount of acid distilled over enough to neutralise this amount of ammonia, and that about as much more should be formed in the destructive distillation of sugar is what would be naturally expected when we consider what are the usual products of distillation of materials poor in nitrogen, such as wood.[1]

TABLE III.

Combustion of Stearin, Oxalic Acid, and Sugar with Soda-lime.

Substance.		Time of Combustion.	Heat of Combustion.	Standard Alkali Solution required to neutralise 1 cc. of Standard Acid.	
Kind.	Weight.			In Standardising.	After Combustion.
	Grams.	Minutes.		cc.	cc.
Stearin, . . .	0.433	115	Medium.	4.34	4.34
" . . .	0.442	70	High.	4.33	4.34
Oxalic Acid, . .	0.408	76	Medium.	4.32	4.33
" . .	0.410	52	High.	4.32	4.33
Sugar, ...	0.401	65	Medium.	4.33	4.23
"	0.399	93	"	4.33	4.19
"	0.487	45	High.	4.31	4.44
"	0.401	45	"	4.31	4.41
"	0.412	45	"	4.33	4.42

Assuming this explanation to be correct, the amounts of nitrogen and acid products are both too small to be of great consequence. The results of these determinations, however, seem to us to help toward an explanation of some of the discrepancies so often observed in the results obtained from the use of sugar in combustions, and to indicate that stearin or oxalic acid is to be preferred for testing the purity of soda-lime.

Apparatus and Manipulation.

Nitrogen bulbs.—For the Knop and Arendt nitrogen bulbs, which, after no little experience with numerous kinds of bulbs and U-tubes, we have, in common with many other chemists, found most satisfactory, we find a slight modification of the ordinary

[1] See accounts of decomposition of sugar by other agencies, and formation of acid products, *e. g.* Conrad and Guthzeit, Ber. deutsch. chem. Ges. 1885, **1**, 439.

form decidedly preferable. This consists in a small bulb of the shape of an ordinary thistle-tube bulb, but of only about 6 or 7 mm. diameter at the outer end in the place of the ordinary point.[1] The great advantage of this is that the acid can be drawn into it directly from the burette, while it offers no impediment to rinsing out completely.

Rinsing the nitrogen bulbs with ordinary distilled water.—Since the distilled water of the laboratory commonly contains small quantities of ammonia, a minute but appreciable error may be introduced when this is employed for rinsing the bulbs before titrating. This error may be made inappreciable by using very small quantities of the water for rinsing. We have found 10 cc. of water sufficient to rinse our Knop and Arendt bulbs, so that no trace of acid or ammonia could be found by further rinsing.

The following results of a test to determine how large the error would be from using a sample of distilled water from the tank in our laboratory, though made simply for our own satisfaction and of no great importance, will perhaps be worth the space they take in print. In each trial one cc. of standard acid was drawn into the nitrogen bulb and poured out again. The bulb was thereafter rinsed in successive trials with varying amounts of the distilled water. When the smaller quantities of the latter were used, water freed from ammonia by redistillation with potassium hydroxide and permanganate, and rejection of so much of distillate as gave a visible reaction with Nessler's reagent, was added to make the volume alike in all. Using the very narrow burettes for measuring and cochineal as an indicator, as was done in the previous experiments, the figures of Table IV were obtained, those for each series representing the averages of practically identical, duplicate results.

TABLE IV.

Number of Trials.	Standard Acid used.	Distilled Water added.	Pure Water added.	Total Solution.	Alkali required to neutralise.
3	1 cc.	10 cc.	90 cc.	101 cc.	4.33 cc.
2	1 "	50 "	50 "	101 "	4.30 "
2	1 "	100 "	none.	101 "	4.26 "

[1] I have an impression that this idea is a German one, but do not recall any description of it, except in catalogues of manufacturers who have made the apparatus in this form in accordance with directions from here.—W. O. A.

As 1 cc. of the standard acid was equivalent to 10 mgm. nearly of nitrogen, the extreme difference, (4.33—4.26) 0.07 cc. of standard alkali, corresponding to the ammonia introduced with 90 cc. of distilled water, would be equivalent to a trifle less than 0.2 mgm. of nitrogen. Unless, therefore, the ammonia in the distilled water should be very much more than in the specimen here used, to heed it in ordinary work would be simply hair-splitting. But where the greatest possible accuracy is required it would seem desirable to at least test the water used, or to use very little. Ordinary well or reservoir water would often be preferable to distilled water for rinsing.

Burettes. Standard acid and alkali solutions. Indicator.—A small quantity of acid in the nitrogen bulb offers less resistance to the passage of the gases, and hence causes less tension inside the combustion tube to expand the latter, than a larger quantity. The smaller the amount of liquid to be titrated the sharper is the reaction. For both these reasons, concentrated solutions seem to us desirable. The great accuracy as well as convenience of very narrow burettes has led us to discard those of ordinary width and to use very narrow ones. For standard acid, a 10 cc. burette graduated to twentieths of a cc., the length from the 0 to 10 mark being about 40 cm., has proved very satisfactory. For the alkali, which may be more dilute than the acid, a somewhat wider burette is convenient. A standard acid of which 10 cc. corresponds to 100 mgm. of nitrogen we find very convenient. If ammonia is used for the alkali, we believe the solution should be titrated against the acid each day it is used, although we have found our standard ammonia solutions to change but very little from month to month.

For an indicator of the neutral point we prefer cochineal to litmus. Besides its commonly urged advantage of being so little affected by carbonic acid, we find that with freshly prepared cochineal solution the change in color from acid to alkaline is very quick and sharp and that the color is more permanent, so that there is less liability to error if the neutralisation is not completed at once. A solution prepared by boiling two grams of commercial cochineal with 100 cc. of water and adding alcohol has proved very satisfactory in our experience. Two drops of this are sufficient to color 100–200 cc. of an acid or alkaline solution.

Length of combustion tubes and method of charging.—As these details have been subjects of no little discussion in connection with the question of the sources of error in the soda-lime method, we give the results of comparative tests made in the course of a series of analyses of flesh of fish. Perhaps the best way to explain the charging of the tube will be by the accompanying tabular statement, in which the figures represent approximate lengths, and are those gradually settled upon after numerous trials with tubes of different lengths and charged in different ways. We intend to have at least forty parts by weight of fine soda-lime for every part of substance in the "mixture." About 0.4–0.6 gram of flesh (water-free), or more in case it contains much fat, we find convenient quantities. Especial stress is laid upon the importance of having the tube so filled with the soda-lime as to leave no considerable open space. The channel, commonly recommended for free passage of the gases, may cause serious error, as will be shown later.

Length of tube,	40 cm.
Asbestos and fine soda-lime,	4 "
Mixture, fine soda-lime and substance,	16 "
Rinsings, fine soda-lime,	4 "
Anterior layer, coarse soda-lime,	12 "
Asbestos, open space, plug,	4 "

A number of comparative trials with larger quantities of soda-lime mixed with the substance to be analysed, sufficient to make the mixture fill about 26 cm. of the tube, gave results practically identical with those obtained when the tubes were charged as here stated.

In the comparative tests with longer anterior layers of soda-lime and correspondingly longer tubes, the charging of the tubes was as just explained, except that while in the ordinary 40 cm. tubes the anterior layer was about 12 cm. long, in the 60 cm. tubes it was approximately 32 cm., and in the 75 cm. tubes nearly 50 cm. The figures of Table V will suffice to show the outcome of a much larger number of trials which they fairly represent. In the cases indicated by the * the "high heat," and in the others the "usual" or "medium heat" (see description of Table III above), was used.

TABLE V.

Comparison of amounts of Nitrogen obtained with longer and shorter combustion tubes.

In Flesh of	Percentages of Nitrogen obtained with tubes of		
	40 cm.	60 cm.	75 cm.
Red Snapper, . . .	...	14.84*	14.80*
Haddock, ...	14.75*	14.76*	14.81*
Flounder, ...	14.13*	14.17*	14.09*
Mackerel, ...	5.82	5.88	
Spanish Mackerel, .	10.75	10.77	
White Perch, . . .	11.82	11.76	
Mascalonge, . . .	13.79	13.85	
White Perch, . . .	13.40	13.44	
Herring, ...	10.19	10.24	
Sheepshead, . . .	11.89	11.91	
Turbot, ...	8.24	8.26	
Pike Perch, . . .	14.66	14.67	
Black Bass, . . .	14.86	14.84	
Lobster, ...	11.85	11.85	
Scallops, ...	10.83	10.85	
Oysters, ...	8.48	8.44	
"	8.84	8.79	
"	7.10	7.05	
"	8.31	8.33	
"	7.85	7.83	
"	9.26	9.22	
"	8.38	8.39	
"	7.15	7.15	

* High heat.

These figures seem to us sufficient to show that in flesh of fish and oysters, at any rate, the difference of 20 cm. or more in the length of the combustion tube, *i. e.* in the length of the anterior layer of soda-lime, does not make any appreciable difference in the amount of nitrogen obtained, provided the above-mentioned precautions are observed and enough of soda-lime is well mixed with the substance, and a moderately long anterior layer of soda-lime, 12–20 cm., is provided. Similar experience with other kinds of animal and vegetable materials, the results of which are scattered through our laboratory note-books, has left us with the very decided impression the same is true of animal and vegetable tissues generally, except in cases to be mentioned hereafter, in which

volatile nitrogenous distillation products are formed and escape ammonification unless unusual precautions are taken. We have often used shorter tubes, from 30 to 35 cm., and have not observed any difference in results, but feel safer with tubes of from 36 to 40 cm. length for ordinary work. But, as will be insisted later, we are persuaded that careful mixing of substance with soda-lime, close packing of the tube, and careful heating, so as to insure complete decomposition of the substance and sufficient contact between distillation products and hot soda-lime, and not too slow conduct of the combustion, are important, otherwise there is danger of loss of nitrogen.

Comparison of Soda-lime and Absolute Methods.

Further observations upon the soda-lime method will be given in succeeding papers. Meanwhile we may here cite some tests of the accuracy of the work by the method just explained, which were made by comparison with the volumetric method. Previous to the making of the volumetric analyses, however, we felt that the method itself needed some examination, not only on account of the need of preliminary practice as a general principle, but because of the sources of error to which determinations are unavoidably exposed. The details of the work were carried out by Dr. J. H. Long, then assistant in this laboratory, and since Professor of Chemistry in Northwestern University and the Chicago Medical College.

The apparatus used and method followed were very similar to those described by Johnson and Jenkins.[1] A few deviations from the method were made, however, of which one was the omission of the potassium chlorate in finishing the combustion. Some minor corrections were also introduced, as detailed beyond. Common experience shows that the absolute method is apt to give rather high percentages of nitrogen. Where the mercury air-pump is depended upon to exhaust the combustion tube, a larger or smaller error in this direction may occur from the incomplete pumping out of the air before the combustion. Various means have been suggested to avoid this. It is sometimes recommended to continue the pumping until the "click" of the mercury in the pump is heard. We have found this hardly sufficient for the most accurate work, and prefer to pump half an hour or so longer, both

[1] This Journal **2**, 28.

before and after the combustion. Even after this a not inconsiderable amount of air remains in the interior of the combustion tube adhering to the glass and contents. A determination in how far an ordinary combustion, such as we were in the habit of making, would be affected by this residual air was attempted by blank combustions in which oxalic acid, previously found to yield no nitrogen (as ammonia) to soda-lime, was employed. Four determinations gave respectively 0.3 cc., 0.6 cc., 0.5 cc. and 0.6 cc. of gas (nitrogen), or on the average 0.5 cc. This quantity was deducted from the volume found in each of the volumetric determinations of nitrogen which follow.

When the nitrogen is collected over potassium hydroxide solution, the vapor tension of the latter may, unless the solution is concentrated, introduce a slight error in the measurement of the gas, as has been observed by Schiff.[1]

Even a 50 per cent. KOH solution gives an appreciable vapor tension, as has been shown by Wüllner.[2] Wüllner's statements are not perfectly clear at first reading, but the facts appear from his formula for the tension, $V = 0.003320\,T - 0.00000432\,T^2$, where V is the decrease of tension for every part of "pentahydrate of potash" to 100 of water (which we understand to be equivalent to $0.51K_2O : 100H_2O$, or 0.51 gram K_2O in 100.51 grams of potassium hydroxide solution).

Dr. Long has made several determinations of the vapor tension of a potassium hydroxide solution of sp. gr. 1.36, using a kathetometer and eudiometer for the purpose. He finds:

Vapor Tension of Potassium Hydroxide Solution of Sp. Gr. 1.36.

At temperature, C.,	6.2	7.1	9.5	14.5
Vapor tension,	2.6 mm.	3.0 mm.	4.0 mm.	6.5 mm.

These results Dr. Long computes to be in accordance with Wüllner's formula. The correction for vapor tension is a small one, but is yet an appreciable quantity.

In the following determinations of nitrogen by the absolute method the charging of the tubes was as indicated below. The total length of the tube was about 80 cm.

CuO. 5 cm.	Fine CuO and substance. 25 cm.	Coarse CuO. 10 cm.	Copper gauze. 10 cm.	Coarse CuO. 10 cm.	$HNaCO_3$, asbestos and stopper about 15–20 cm.

[1] Zeitsch. f. Anal. Chem. **7**, 432. See also Kreussler, Landw. Vs. St. **31**, 236.
[2] Pogg. Annalen **110**, 1860, 570.

Corrections for residual air (nitrogen) in the combustion tube and for vapor tension of sodium hydroxide solution were made as above described; the latter correction, however, is applied separately to the percentages of nitrogen in Tables VI and VII herewith, to show more plainly its effect on the result. It is superfluous to add that the nitrogen was measured in a calibrated eudiometer and that the corrections for temperature and barometric pressure were made in the ordinary manner.

TABLE VI.

Nitrogen in Pure Ammonium Oxalate.

	A.	B.	C.
Ammonium oxalate taken	0.5000 grm.	0.6000 grm.	0.6000 grm.
Volume of N found,	79.2 cc.	94.6 cc.	94.4 cc.
Weight of N found,	0.0995 grm.	0.1189 grm.	0.1186 grm.
Per cent. of N found,[1]	19.90 per ct.	19.82 per ct.	19.77 per ct.
Per cent. of N corrected,[2]	19.84 "	19.75 "	19.71 "

TABLE VII.

Nitrogen in Pure Ammonium Sulphate.

	A.	B.	C.	D.
Ammonium sulphate taken,	0.6000 gram.	0.6000 gram.	0.6000 gram.	0.6000 gram.
Volume of N found,	102.0 cc.	101.5 cc.	102.0 cc.	101.8 cc.
Weight of N found,	0.1282 gram.	0.1275 gram.	0.1281 gram.	0.1279 gram.
Per cent. of N found[1]	21.36 per ct.	21.25 per ct.	21.35 per ct.	21.32 per ct.
Per ct. of N corrected[2]	21.24 "	21.16 "	21.29 "	21.25 "

The average percentages of nitrogen in the ammonium salts, as above obtained, compare with those found by combustion with soda-lime and with the theoretical percentages as below. The determinations by the soda-lime method are given in detail in another place.

TABLE VIII.

Comparative Percentages of Nitrogen.

	In Ammonium Oxalate.	In Ammonium Sulphate.
Found by absolute method,	19.77 per cent.	21.24 per cent.
Found by soda-lime method,	19.76 "	21.21 "
Theoretical,	19.72 "	21.21 "

[1] Corrected for residual air in tube, temperature and pressure.

[2] Corrected for vapor tension of KOH solution.

The following are comparative results of determinations of nitrogen in flesh (mainly muscular tissue) of fish. Those with soda-lime were made by one of us (W.),[1] those by the absolute method by Dr. Long. Neither knew the results of the other's work until after both had been recorded upon the laboratory books.

TABLE IX.

Comparison between Percentages of Nitrogen found by Soda-lime and Absolute Methods in Flesh of Fish, etc.

In Flesh of	Soda-lime.			Absolute.
	A	B	Average.	
	Per cent.	Per cent.	Per cent.	Per cent.
Fish, Mackerel, ...	5.88	5.82	5.85	5.96
" Spanish Mackerel, .	10.77	10.75	10.76	10.68
" Mascalonge, . . .	13.85	13.79	13.82	13.91
" Herring, ...	10.24	10.19	10.21	10.22
" Sheepshead, . . .	11.89	11.91	11.90	11.95
" Black Bass, . . .	14.84	14.86	14.85	14.87
Lobster, ...	11.85	11.85	11.85	11.78
Scallops, ...	10.85	10.83	10.84	10.83

The outcome of these observations, and especially the close agreement of the results obtained with the two different methods, by analysts working entirely independently of each other and with no knowledge of each other's results until they were tabulated together, persuaded us that our determinations by the soda-lime method were of sufficient accuracy to meet the demands of the investigation of the composition of animal tissues, to which they were preparatory.

At the same time we are very far from saying that we regard the soda-lime method as entirely reliable, even for protein compounds, unless all needed precautions are observed.

The recapitulation of the points here urged will come appropriately in subsequent articles, which will discuss some of the sources of error in the soda-lime method and means for avoiding them.

[1] In connection with Mr. Miles Beamer.

Contributions from the Chemical Laboratory of Harvard College.

LII.—ON BENZOLTRISULPHONIC ACID.[1]

By C. Loring Jackson and John F. Wing.

Benzoltrisulphonic acid has been prepared up to this time only by Senhofer,[2] who made it by heating a mixture of benzol, fuming sulphuric acid, and phosphoric pentoxide to 280°–290° in a sealed tube, and studied its potassium, barium, lead, and silver salts, while in a subsequent paper[3] he made a thorough investigation of the action of melted potassic hydrate upon it—a large amount of work when the extreme difficulty of the method of preparation is considered.

Our attention was first drawn to this substance while we were trying to make potassic benzolparadisulphonate by the method of Barth and Senhofer,[4] and encountered in one preparation large well-formed crystals, giving with phosphoric pentachloride a chloride melting above 180°, which proved on analysis to be Senhofer's potassic benzoltrisulphonate. As we could find no mention of the appearance of the trisulphonate under these conditions in the papers of Barth and Senhofer,[4] Koerner and Monselise,[5] or of any other chemists who have studied the action of sulphuric acid on benzol, we searched for the cause of this abnormal result, and soon found it in the fact that we had heated the crude potassic disulphonate a second time with fuming sulphuric acid. After this a few experiments were enough to prove that the action was due to the presence of potassic sulphate, and, to our great surprise, that common sulphuric acid in presence of potassic sulphate was capable of converting a benzolsulphonic acid into the trisulphonic acid, and was as efficient in this respect as the fuming sulphuric acid.

This result, it seems to us, throws light on the beautiful method of preparing trisulphonic acids, the application of which to toluol was published by Claësson[6] in 1881, and which consists in heating

[1] Communicated by the authors from the Proceedings of the American Academy of Arts and Sciences.

[2] Annalen der Chemie **174**, 243.

[3] Wien. Acad. Ber., Ser. 2, **78**, 677.

[4] Berichte der deutsch. chem. Gesell. **8**, 1478.

[5] Gazz. Chim. 1876, 133.

[6] Berichte der deutsch. chem. Gesell. **14**, 307.

a potassic sulphonate with chlorsulphonic acid, since it makes it probable that the reaction is due to the acid potassic sulphate formed during the process, rather than to the chlorsulphonic acid itself. In a general way also our process resembles that of Neville and Winther[1] for converting the amido compounds into their monosulphonic acids by the action of heat on their acid sulphates, although it is doubtful whether the mode of action of the two processes is the same, since in ours the presence of an excess of sulphuric acid is essential.

As our process converts benzoltrisulphonic acid from one of the least into one of the most accessible of the less common aromatic compounds, we have devoted some time to its study, and in this paper, after giving the details of our preliminary experiments, and the methods for preparing the benzoltrisulphonic acid, we describe the first results that we have obtained; which consist of the determination of the crystalline form and solubility of the potassium salt,[2] the preparation and study of the chloride, the ester, which exhibits a strange instability, the amide, with several of its metallic derivatives, and its benzoyl compound, and as this, like the corresponding compound of the benzolmonosulphamide, is an acid, its sodium and barium salts and chloride with the phenylamidine derived from it, the anilid, and finally the proof by two different methods that the benzoltrisulphonic acid has the symmetrical constitution 1, 3, 5.

Formation of Benzoltrisulphonic Acid.

To prove that the presence of potassic sulphate was the cause of the formation of the trisulphonic acid, a solution of benzol in fuming sulphuric acid, to which its own volume of common sulphuric acid had been added, was divided into two equal parts (*a*) and (*b*), and, after adding a quantity of potassic sulphate to (*a*), both parts were heated in retorts under precisely the same conditions until half of the liquid had passed over. The residues were converted into potassium salts, and recrystallised, when (*a*) furnished the very characteristic crystals of the potassic benzoltrisulphonate, and gave a chloride which, after washing with ether and one crystallisation from chloroform, melted at 182° [$C_6H_3(SO_2Cl)_3$ melts at 184°], proving that the trisulphonic acid had

[1] Berichte der deutsch. chem. Gesell. **13**, 1940.

[2] Also some attempts to prepare substituted trisulphonic acids, which led to negative results.

been formed, while (*b*) gave a potassium salt crystallising in an asbestos-like[1] mass, which yielded a viscous chloride, from which no trace of the benzoltrisulphochloride could be obtained; and, as both the potassic benzoltrisulphonate and its chloride are very characteristic substances, there can be no doubt that in this latter case no appreciable amount of the trisulphonic acid was formed. In a second experiment the benzolmetadisulphonic acid (made by heating the chloride with water to 150° in a sealed tube) was used, and the result was the same; the specimen heated with sulphuric acid and potassic sulphate gave benzoltrisulphonic acid recognised as in the previous experiment, while that heated with sulphuric acid alone gave no trace of this product.

The experiments just described having proved that the presence of potassic sulphate is necessary for the formation of the trisulphonic acid, we next considered the question, "Cannot the trisulphonic acid be formed by the action of acid potassic sulphate alone without an excess of sulphuric acid?" and found that potassic benzolmetadisulphonate fused with acid potassic sulphate remained unaltered, even at a temperature where the mass began to char. It is evident, therefore, that the potassic sulphate serves only to render the sulphuric acid more efficient, and it remained to determine by experiment, if possible, the manner of its action. Since in Senhofer's method, the only one beside ours by which the benzoltrisulphonic acid has been obtained, the action was due to the presence of a powerful dehydrating agent (phosphoric pentoxide), the most plausible theory was that the acid potassic sulphate acted simply by the removal of water. To test this hypothesis we substituted for the potassic sulphate in one experiment argentic sulphate, and in another zincic sulphate, as, if the action of the salt is due only to its attraction for water, like that of the phosphoric pentoxide in Senhofer's method, the latter should produce quite as good a result as potassic sulphate, whereas the argentic sulphate would be entirely without action. Upon heating three portions of benzolmetadisulphonic acid with the same proportion of sulphuric acid, (*a*) without the addition of a salt, (*b*) with addition of zincic sulphate, and (*c*) with addition of argentic sulphate, we found that, while no trace of the trisulphonic acid could be detected in (*a*)

[1] We have not succeeded in determining the nature of this potassium salt. It does not resemble the potassic benzolmonosulphonate, which crystallises in glistening plates, nor have we found any disulphonate corresponding to it in properties. We hope to return to this subject hereafter.

or (*b*), it was formed in large quantity in (*c*), and, if anything, was accompanied with less of the tarry secondary products than when potassic sulphate was used, so that argentic sulphate could perhaps be used advantageously in place of potassic sulphate in the manufacture of the trisulphonic acid, since, owing to its slight solubility, it can be filtered out with little loss after the addition of water to the product of the reaction, and is then ready to use again after drying. It follows from the above results that the salt does not act as a dehydrating agent, but rather as a carrier of the sulphuric acid, owing to the formation of an acid salt.

The experiments just described have led us to the following hypothesis to explain the formation of the benzoltrisulphonate by the action of potassic sulphate and sulphuric acid; but we wish it distinctly understood that we could find no way of submitting this hypothesis to a complete experimental proof, and therefore offer it simply as the most plausible explanation of the observed facts that we have been able to find. The acid potassic sulphate formed by the sulphuric acid and potassic sulphate is first, we suppose, converted into the potassic pyrosulphate by loss of water, and the pyrosulphate in its turn decomposed by the sulphuric acid, giving potassic sulphate and fuming sulphuric acid, which, breaking up into H_2SO_4 and SO_3, furnishes the nascent sulphuric anhydride to form the benzoltrisulphonic acid, while the potassic sulphate goes through the same series of reactions again, which can be written as follows:

$$K_2SO_4 + H_2SO_4 = 2KHSO_4,$$
$$2KHSO_4 = K_2S_2O_7 + H_2O,$$
$$K_2S_2O_7 + H_2SO_4 = K_2SO_4 + H_2S_2O_7 = K_2SO_4 + H_2SO_4 + SO_3.$$

Of these reactions the second can be considered well established, since the proportion of acid to potassic sulphate in the mixture used by us is almost exactly one molecule of K_2SO_4 to two of H_2SO_4; and it has been found,[1] when such a solution is allowed to cool, that it deposits first the neutral salt K_2SO_4, and afterward the potassic pyrosulphate $K_2S_2O_7$. But the last reaction is certainly not above criticism, since in it sulphuric acid is made to displace pyrosulphuric acid, which last, it is fair to suppose, is the stronger of the two. In answer to this we would suggest, that the reaction either may be brought under Berthollet's law on account of the formation of the volatile sulphuric anhydride, or,

[1] Gmelin Kraut's Handbuch der Chemie, 1875, **2**, 48.

what seems to us more probable, it is brought about by the concurrent attraction of the sulphuric anhydride for the benzoldisulphonic acid. It is possible, however, that one of the two following reactions may express the action more correctly:

$$KHSO_4 + C_6H_4(SO_3H)_2 = C_6H_3(SO_3H)_2SO_3K + H_2O.$$
$$K_2S_2O_7 + 2C_6H_4(SO_3H)_2 = 2C_6H_3(SO_3H)_2SO_3K + H_2O.$$

But in these reactions the excess of sulphuric acid must be supposed to act as a dehydrating agent, and thus produce the action, since we have proved experimentally that no action takes place when an excess of sulphuric acid is absent; and this observation seems to us to make these two reactions less probable than the series in which sulphuric anhydride is formed.

We have not multiplied experiments with different metallic sulphates, as it has not seemed to us that such work would throw any additional light on the theory of the process; we may mention, however, that we have also tried aluminic sulphate, which gave rise to the formation of a little trisulphonate when heated with metadisulphonic acid and sulphuric acid, but, as far as we could judge, was much less efficient in its action than the potassic sulphate.

Preparation of Benzoltrisulphonic Acid.

As the result of many experiments we have worked out the following process for preparing benzoltrisulphonic acid from potassic benzolmetadisulphonate. 15 grams of potassic benzolmetadisulphonate, which need not be freed from its water of crystallisation, are mixed in a porcelain dish with 18 grams of common strong sulphuric acid,[1] and heated with the free flame, care being taken to avoid heating the edges of the liquid too intensely during the first stage of the process, as at this time there is danger of charring. After the salt has dissolved, the sulphuric acid begins to come off in heavy white fumes, but without the formation of bubbles; in fact, there is no bumping or tumultuous evolution of vapor in any part of the process. If the operation is stopped at this point, the disulphonate will be found unaltered. After heating for a few minutes, little bubbles appear in large numbers, and soon after the mass becomes pasty, and begins to puff up, while the evolution of fumes slackens; at this point the lamp is to be removed. The product, if

[1] Double these quantities can be used, but it is not convenient to work with much larger quantities than 30 grams at a time. The benzolmetadisulphonate may contain a small quantity of potassic carbonate or sulphate without injury to the process, but should be free from colored tarry impurities.

charring was avoided in the early part of the process (there is little danger of it later), is of a reddish brown color, and almost completely solid. The loss in weight should be about 7 grams, and the whole operation takes little more than fifteen minutes. After the residue is cold, it is dissolved in water, and treated with an excess of baric carbonate to remove sulphuric acid, when the greater part of the colored impurity is carried down by the baric sulphate, so that the filtrate is usually of a pale wine-yellow. The precipitate should be boiled out with water once or twice, and the washings added to the filtrate, which, after converting any barium salt into potassic trisulphonate by potassic sulphate, is evaporated until its surface after cooling is covered with little crystals, when it usually deposits fine crystals after a short time, which can be increased in size by the spontaneous evaporation of part of the mother liquor, and purified by recrystallisation from boiling water. The mother liquors, when sufficiently concentrated, solidify to a brownish pasty mass of a finely granular consistency, filled with larger crystals of potassic benzoltrisulphonate, which can be separated mechanically by scraping with a flat-pointed platinum stirrer the semi-liquid finer grained impurity through the holes in a perforated platinum cone placed in a funnel. The larger crystals left behind are then purified by crystallisation from water. The yield from this process can be raised by careful work to 44 per cent. of the theoretical yield, and it is possible to increase it still further by boiling the precipitate formed by baric carbonate with a solution of potassic carbonate, as the baric benzoltrisulphonate is very sparingly soluble in water. We cannot recommend this treatment, however, as the potassic benzoltrisulphonate extracted in this way is contaminated to such an extent with the colored impurities carried down by the precipitate of barium salts, that it is very hard to obtain white and pure crystals from it; in fact, it is easier to prepare fresh from the benzolmetadisulphonate.

The benzoltrisulphonic acid can also be prepared from benzol without isolating the lower sulphonic acids, and this method is sometimes convenient when large quantities of the substance are desired; but it is decidedly inferior to that just described, for two reasons, first, because the yield is very much smaller, and, second, a certain amount of benzolparadisulphonate is formed, which it is not easy to separate from the trisulphonate by crystallisation. For this purpose 100 (or more) grams of benzol are dissolved in the

same volume of common sulphuric acid by boiling them together in a flask with a reverse cooler;[1] when the solution is complete, the product is mixed with its own volume of common sulphuric acid and between 60 and 70 grams of potassic sulphate, and distilled in an untubulated retort till about one-third of the total amount of sulphuric acid used has passed over. The liquid boils quietly without bumping. The residue is then divided into two parts, and these are heated in porcelain dishes precisely as in the previous process. The product is much more impure than when made from the potassic disulphonate, and it is better therefore to decolorise it by treatment with plumbic oxide after a part, but not the whole, of the large excess of sulphuric acid has been removed by marble or baric carbonate, since the greater part of the coloring matter is precipitated on adding an excess of plumbic oxide if the solution is acid, and still more comes down with the plumbic carbonate when potassic carbonate is added to the filtrate; but if the solution is thoroughly neutralised by the marble, very little, if any, of the colored impurity comes down with the lead salts, and in that case it is very hard to get rid of it. The yield was very small, and, although we could have raised it undoubtedly by working up the insoluble residues, we have never tried to do so, because we have found it easier to prepare a fresh portion than to purify the highly colored salts which would be obtained in this way. It is advisable, however, to heat once more with sulphuric acid the brown impure residues left by the evaporation of the mother liquors, from which no more crystals of benzoltrisulphonate can be separated, as in this way an additional quantity of the trisulphonate can be obtained. We have tried also to purify the impure residues left after the removal of the crystals by treatment with phosphoric pentachloride, and washing the product with ether or chloroform, but have obtained only unsatisfactory results.

The secondary products formed in this process are of little or no interest. They consist principally of a dark reddish brown to black substance giving a potassium salt of tarry consistency more soluble than the potassic benzoltrisulphonate, which it will not be easy to purify. There appears also on evaporation of the mother liquors a dark-colored granular potassium salt, whose viscous chloride solidifies after standing for some weeks, and it is then possible to obtain much benzoltrisulphochloride from it by treatment with chloroform; it is probable, therefore, that it consists

[1] Michael and Adair, Berichte der deutsch. chem. Gesell. **10**, 585.

principally of the benzoltrisulphonate prevented from crystallising by the presence of the dark-colored impurity just mentioned, or of some potassic benzolmetadisulphonate.

If the trisulphonic acid was made direct from the monosulphonic acid, some benzolparadisulphonic acid was also formed, which made the purification of the benzoltrisulphonate by crystallisation more difficult. It was recognised by the melting point of its chloride, 139°, whereas Koerner and Monselise[1] give 131°, and the following analysis of the chloride dried at 100°:

0.1008 gram of substance gave, after decomposition by boiling with a solution of pure sodic carbonate, 0.1054 gram of argentic chloride.

	Calculated for $C_6H_4(SO_2Cl)_2$.	Found.
Chlorine	25.82	25.86

We are inclined to consider the melting point (139°) given by us for the benzolparadisulphochloride as more accurate than that of Koerner and Monselise (131°), since their product was prepared from a mixture of the para and meta compounds, and a small quantity of the latter, melting at 63°, would have been enough to lower the melting point very considerably, and its presence could not be determined by analysis; the impurity in our product, on the other hand, would have been benzoltrisulphochloride, and that there could have been no appreciable amount of this substance present is shown conclusively by our analysis.

Benzoltrisulphonic Acid and its Salts.

We have little to add under this head to the excellent work of Senhofer. The free acid, when heated, became charred, and gave off a smell like caramel; but the soluble part of the residue consisted of the unaltered acid, as was shown by the crystalline form of its potassium salt and the melting point of its chloride. The experiment gave so little promise of interesting results that it was not repeated on a larger scale. The following analysis of the free acid dried at 100°, which it was necessary to make in the course of our work, confirms Senhofer's statement that it retains three molecules of water at that temperature.

0.3772 gram of the acid dried at 100° gave by the method of Carius 0.7004 gram of baric sulphate.

	Calculated for $C_6H_3(SO_3H)_3\,3H_2O$.	Found.
Sulphur	25.80	25.51

[1] Gaz. Chim. 1876, 140.

We add also an analysis of the potassium salt, which yielded the same amount of water of crystallisation (three molecules) as given by Senhofer; but, whereas he states that only one and a half molecules of the water are given off at 100°, we found that the whole was evolved at this temperature.

0.3768 gram of air-dried salt at 100° lost 0.0431 gram.

	Calculated for $C_6H_3(SO_3K)_3\,3H_2O$.	Found.
Water	11.11	11.43

0.7404 gram of dry salt gave 0.442 gram of potassic sulphate.

	Calculated for $C_6H_3(SO_3K)_3$.	Found.
Potassium	27.13	26.80

We have determined the solubility of the potassium salt as follows:

I. 3.6594 grams of a solution of $C_6H_3(SO_3K)_3$ saturated at 20° left on evaporation 1.3074 grams of the salt dried at 260°.

II. 2.034 grams of the solution gave 0.716 gram of the dried salt.

Therefore a saturated solution of potassic benzoltrisulphonate at 20° contains the following percentages of the salt free from water of crystallisation:

I.	II.
35.72	35.21

Dr. O. W. Huntington has at our request determined the crystalline form of the potassium salt $C_6H_3(SO_3K)_3\,3H_2O$, and kindly furnishes us with the following statement:

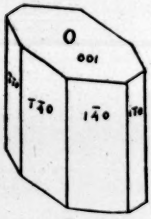


FIG. 1.

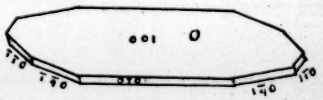


FIG. 2.

"Monoclinic, with marked variation of type. As no planes were observed except the basal plane and vertical domes, and pinacoids, it was impossible to make a complete determination of the crystal. The following measurements were obtained:

$$001 \wedge 1\bar{1}0 = 65° 28'$$
$$1\bar{1}0 \wedge 110 = 50° 55'$$
$$1\bar{1}0 \wedge 1\bar{4}0 = 24° 40'$$
$$1\bar{4}0 \wedge 140 = 79° 45'$$

Most of the faces of the crystals were uneven, and the angles printed in heavy type are the only ones which could be measured with accuracy.

"From these angles the inclination of the axes and the ratio of the ortho diagonal to the clino axis may easily be calculated.

$$\beta = 68° 38' 30'' \qquad a : b = 1 : 2.10.$$

The crystals vary between the form shown in Fig. 1 and that of Fig. 2. In the second form the clino pinacoid is a characteristic feature which is absent in crystals of the first type, and the forms of both types run out into needles, in one case parallel to the vertical axis, and in the other parallel to the clino diagonal."

The potassium salt is not acted on by a cold solution of potassic permanganate, but, if heated with it, is oxidised, and we were unable to find any organic matter in the product.

The following attempts were made to obtain substituted benzoltrisulphonic acids. The silver salt was made by boiling the chloride with argentic oxide and water, and to the filtered solution bromine was added in order to make brombenzoltrisulphonic acid by the method of Nölting and Plawski,[1] which has been proved to be of wide application to monosulphonic acids by Limpricht.[2] A heavy precipitate of argentic bromide was formed at once, but the filtrate after being freed from compounds of bromine by evaporation gave a chloride melting at 184°, the melting point of benzoltrisulphochloride. It was analysed also, as it was barely possible that the brombenzoltrisulphochloride might melt at the same temperature as the non-substituted compound.

0.2374 gram of the substance gave 0.2718 gram of argentic chloride.

	Calculated for $C_6H_3(SO_2Cl)_3$.	Found.
Chlorine	28.52	28.32

The argentic benzoltrisulphonate, therefore, is affected by bromine in an entirely different way from the monosulphonates. The

[1] Berichte der deutsch. chem. Gesell. **8**, 819. [2] Annalen der Chemie **188**, 134.

filtrate before evaporation contained bromic acid, as was proved by the following experiments. Some of the filtrate containing no free bromine gave no precipitate when argentic nitrate was added, but upon boiling with alcohol a heavy precipitate of argentic bromide was formed; to another portion of this filtrate potassic iodide was added, when iodine was set free in large amount. The reaction must run as follows:

$$C_6H_3(SO_3Ag)_3 + 3Br_2 + 3H_2O = 3AgBr + C_6H_3(SO_3H)_3 + HBrO_3 + 2HBr.$$

Iodine acts on the argentic benzoltrisulphonate in a similar way. We have tried also to obtain a bromine compound by heating the potassium salt with bromine to 140° for sixteen hours, and also by heating it dissolved in strong sulphuric acid with bromine; but in neither case was hydrobromic acid given off, the trisulphonic acid remaining unaltered. It is possible, however, that longer heating with bromine might produce the desired result.

Our attempts to obtain a nitro acid were no more successful than those to make the bromine acid, as the potassic benzoltrisulphonate can be boiled with fuming nitric acid, or even with a mixture of fuming nitric acid and sulphuric acid, for over an hour without undergoing any alteration. When, however, the chloride is heated to 140° for sixteen hours with a large excess of fuming nitric acid, it is converted into a new substance with the most uninviting properties, which we have not studied further because sulphuric acid is eliminated in the process, and we propose to confine our attention to the trisulpho compounds.

Benzoltrisulphochloride, $C_6H_3(SO_3Cl)_3$.

This substance is prepared by heating potassic benzoltrisulphonate, previously dried at 150°, with a little more than the calculated amount of phosphoric pentachloride (10 parts of the salt to 15 of the pentachloride) in a test-tube or flask to 150° in an air-bath. If the substances are heated in a dish there is little or no action. After the phosphoric oxychloride has distilled off, the product is treated with water, and finally warmed with it, but this warming should not be long continued, as the trisulphochloride is much more easily attacked by hot water than the benzolmetadisulphochloride. After washing the chloride thoroughly with warm water, it is purified by crystallisation from boiling chloroform. The

yield was between 80 and 90 per cent. of the theoretical. Samples contaminated with lower sulphochlorides often can be freed from them by washing with ether. The substance dried at 100° gave the following results on analysis:

I. 0.2984 gram gave, after decomposition by boiling with a solution of potassic hydrate, 0.3488 gram of argentic chloride.

II. 0.1300 gram treated in the same way gave 0.1530 gram of argentic chloride.

III. 0.2374 gram gave, after decomposition with a boiling solution of pure sodic carbonate, 0.2718 gram of argentic chloride.

	Calculated for $C_6H_3(SO_2Cl)_3$.	Found. I.	II.	III.
Chlorine	28.52	28.90	29.10[1]	28.32

Properties.—The benzoltrisulphochloride crystallises from chloroform in little silky flattened needles, which under the microscope are seen to have the ends bevelled, or occasionally terminated by two planes forming an obtuse angle; frequently groups are observed made up of a number of needles united longitudinally, giving a characteristic comb-like appearance to the ends. Out of benzol it forms good-sized plates, apparently belonging to the triclinic system. It melts at 184° (uncorr.), and sublimes with some difficulty at temperatures above 200°, forming good-sized flattened needles similar in shape to the crystals from benzol. It is insoluble in water, hot or cold, but is slowly decomposed and dissolved when boiled with it; very slightly soluble in cold alcohol or methyl alcohol, but freely dissolved with decomposition when boiled with them; very slightly soluble in ligroin, slightly soluble in ether, freely in benzol, carbonic disulphide, glacial acetic acid, or chloroform. Chloroform is the best solvent for it, as it is much more soluble in it when hot than when cold. As already mentioned, the chloride is slowly converted into the acid by boiling water, and is much more easily attacked in this way than the benzolmetadisulphochloride, so that the acid can be prepared conveniently by heating it with water in open vessels, whereas with the di compound this reaction does not take place readily at temperatures below 140°. With boiling alcohol the product is also the acid; but this point will be discussed more fully under the ester. Solutions of potassic hydrate or carbonate, or a mixture of argentic oxide and water, when boiled with the chloride, convert it quickly and

[1] The potassic hydrate used in I and II was not perfectly free from potassic chloride.

easily into the corresponding salt. The study of the action of reducing agents on the chloride will be reserved for a future paper.

Benzoltrisulphonic Ester, $C_6H_3(SO_3C_2H_5)_3$.

This substance was prepared by the action of ethyl iodide on argentic benzoltrisulphonate, made by boiling the chloride with argentic oxide, and after filtering out the argentic chloride and excess of argentic oxide, evaporating to dryness on the water-bath, and drying at 100°. The ethyl iodide acts on the silver salt with violence even in the cold, so that the process must be carried on in a flask with a return condenser, and, after it has come to an end, which can be made sure by heating for a short time on the water-bath, the product is extracted with ether, and the extract purified by crystallisation from benzol, and dried in vacuo. Ethyl bromide may be used instead of ethyl iodide, but in this case the mixture must be heated to 100° in a sealed tube to obtain complete action.

The ester can also be prepared by the action of benzoltrisulphochloride, mixed with a large excess of benzol, on the proper amount of sodic ethylate made from as little alcohol as possible; but this method is not so good as the preparation from the silver salt and ethyl iodide. If the attempt is made to prepare the ester by the action of sodic ethylate dissolved in alcohol upon the benzoltrisulphochloride, the product is sodic benzoltrisulphonate, or, if absolute alcohol is substituted for sodic ethylate, benzoltrisulphonic acid, the ester at first formed being afterward decomposed by the absolute alcohol, according to the reaction given under the properties of the ester. The ester cannot be made by the action of hydrochloric acid gas on an alcoholic solution of the trisulphonic acid. The composition of the ester dried in vacuo was determined by the following analysis:

I. 0.2646 gram of the substance gave by the method of Carius 0.4662 gram of baric sulphate.

II. 0.156 gram of the substance gave 0.2719 gram of baric sulphate.

	Calculated for $C_6H_3(SO_3C_2H_5)_3$.	Found. I.	Found. II.
Sulphur	23.88	24.16	23.94

Properties.—The benzoltrisulphonic ester forms well-developed shining white crystals, often more than a centimeter long, which belong to the triclinic system; a careful measurement of their

angles was, however, impossible, because we could not obtain them with smooth enough faces. It melts at 147°, but if heated for some time to 110° is decomposed, leaving a residue of the benzoltrisulphonic acid; the reaction which takes place is probably the following:

$$C_6H_3(SO_2C_2H_5)_3 = C_6H_3(SO_2H)_3 + 3C_2H_4,$$

as 0.1674 gram of substance lost 0.0324 gram.

Calculated for a loss of $3C_2H_4$.	Found.
20.89	19.36.

It is essentially insoluble in water, freely soluble in ether, chloroform, carbonic disulphide, or benzol—the last being the best solvent for it—insoluble in ligroin, decomposed and dissolved by glacial acetic acid, dissolves freely in alcohol, but is decomposed by it, as upon evaporating the solution, even if absolute alcohol is used, the benzoltrisulphonic acid is left. This reaction seemed to us so curious that we studied it more carefully, as follows. 10 grams of benzoltrisulphochloride were boiled in a flask with a reverse cooler with 12 grams of absolute alcohol; after half an hour the solid had completely dissolved, and upon examining the flask it was found that much hydrochloric acid had been formed, also apparently a little ethyl chloride due to a secondary reaction, but no ethylene could be detected. The contents of the flask, after being freed from hydrochloric acid with potassic hydrate, were distilled fractionally with a Hempel's column, when it appeared that the principal product of the reaction was ethyl-ether, recognised by its boiling point, 35°, and by its smell. The following reactions, therefore, probably take place:

I. $C_6H_3(SO_2Cl)_3 + 3C_2H_5OH = C_6H_3(SO_2C_2H_5)_3 + 3HCl$;

II. $C_6H_3(SO_2C_2H_5)_3 + 3C_2H_5OH = C_6H_3(SO_2H)_3 + 3(C_2H_5)_2O$;

and the action is exactly analogous to the ordinary method of making ethyl ether. Methyl alcohol seems to act on the ester in the same way as ethyl alcohol—the residue left after evaporating a methyl alcohol solution of it being benzoltrisulphonic acid. The ester was not acted on in the cold by sodium or sodic ethylate.

Benzoltrisulphamide, $C_6H_3(SO_2NH_2)_3$.

This substance was made by adding a very strong solution of ammonia to the benzoltrisulphochloride and allowing the mixture to

stand a short time. It was purified by crystallisation from boiling water. It can be formed also by the action of ammonic carbonate on the chloride, but the result was less satisfactory than with the solution of ammonia. The mother liquors from the crystallisation contain a quantity of ammonic benzoltrisulphonate, which, after conversion into the potassium salt by boiling with potassic hydrate, can be reconverted into the chloride. The substance dried at 100° gave the following results on analysis:

I. 0.2358 gram of substance gave after heating with soda-lime 0.1162 gram of ammonic chloride.

II. 0.3739 gram of substance gave, according to the method of Carius, 0.8318 gram of baric sulphate.

	Calculated for $C_6H_3(SO_2NH_2)_3$.	Found. I.	II.
Nitrogen	13.33	12.89	...
Sulphur	30.47	...	30.56

Properties.—The benzoltrisulphamide crystallises from boiling water in shining flattened needles with very sharp ends, sometimes nearly a centimeter long. It can also be obtained from water in square prisms with oblique ends, apparently of the monoclinic system, or in rhombic plates. From alcohol it crystallises in long slender needles. Its melting point is 310°–315° (uncorr.); it is only slightly soluble in cold water, as shown by the following determination of its solubility:

I. 12.367 grams of the solution saturated at 25° gave on evaporation 0.0172 gram of the amide.

II. 11.164 grams of the solution gave 0.0186 gram of the amide.

The solution of the benzoltrisulphamide saturated at 25° contains, therefore,

I.	II.
0.14 per cent.	0.17 per cent.

It is much more freely soluble in boiling water than it is in cold, and this is the best solvent for it; soluble in alcohol, rather more so in methyl than in common alcohol; not very soluble in benzol; insoluble, or nearly so, in ether, ligroin, chloroform, or glacial acetic acid either hot or cold. The amide is much more soluble in a solution of ammonia than in water, but it is thrown down unaltered when the ammonia is driven off from such a solution by heat; it also dissolves very easily in a solution of potassic hydrate, and this solution is not decomposed, even when it is boiled for a

short time. The hot aqueous solution of the amide gives a white precipitate with mercuric nitrate, but none with mercuric chloride; a difference in behavior which is not surprising when it is remembered how differently these two reagents act with acid sodic carbonate, sodic phosphate, oxalic acid, and even water. The composition of the precipitate formed with mercuric nitrate is discussed below. The hot solution of the amide also gives with mercurous nitrate a white precipitate, which becomes gray on standing, but no precipitate with solutions of the salts of any of the other common metals.

The *Silver Salt*, $C_6H_3(SO_2NHAg)_3$, was made by adding argentic nitrate to a hot solution of the amide, and then ammonic hydrate, but not in excess, as this dissolves the precipitate; if by accident an excess has been added, the precipitate can be obtained again by boiling off the ammonia. The flocculent white precipitate thus formed was washed with water, dried in vacuo, and analysed.

0.2778 gram of the salt gave by precipitation from its solution in dilute nitric acid 0.1886 gram of argentic chloride.

	Calculated for $C_6H_3(SO_2NHAg)_3$.	Found.
Silver	50.94	51.11

It is a tolerably stable white powder, insoluble in water, soluble in nitric acid or ammonic hydrate. When a little tincture of iodine is added, the silver is converted into argentic iodide. Compare the analogous reaction with mercuric salt.

Mercuric Salts of Benzoltrisulphamide.—When the amide is boiled with yellow mercuric oxide suspended in water, a white precipitate is formed, the composition of which varies according to the proportion of oxide and amide used.

$C_6H_3(SO_2NHHgOH)_3$.—To prepare this salt, 0.65 gram of mercuric chloride was converted into the oxide by precipitation with sodic hydrate, and the washed but not dried oxide boiled with a solution of 0.25 gram of the amide. The action takes place very slowly even under these conditions (much more slowly and imperfectly if the oxide has been dried); but after boiling for twenty-four hours it was nearly complete, although there were still a few yellow specks of oxide visible. These were separated mechanically, as far as possible, and the precipitate washed and dried at 100°; its analysis is given under I. The same salt is

obtained much more conveniently by adding a solution of mercuric nitrate to a boiling solution of the amide, and washing with boiling water. An analysis of the salt thus prepared, and dried at 100°, is given under II. It is probable that the mercuric nitrate forms at first the compound $C_6H_3(SO_2NHHgNO_3)_3$, and that this is decomposed by the hot water in the same way that mercuric nitrate itself is. We do not pretend to determine, however, whether the hydroxyl is attached to the mercury or to the nitrogen, which in the latter case would be in the quinquivalent condition.

I. 0.299 gram of substance dissolved in hydrochloric acid and treated with sulphuretted hydrogen gave 0.2164 gram of mercuric sulphide.

II. 0.2756 gram of substance gave 0.1994 gram of mercuric sulphide.

	Calculated for $C_6H_3(SO_2NHHgOH)_3$.	Found. I.	Found. II.
Mercury	62.30	62.38	62.38

$[C_6H_3(SO_2NH)_3]_2Hg_3$.—This salt was prepared like the preceding, by boiling the moist mercuric oxide from 0.65 gram of mercuric chloride with 0.5 gram of the amide in aqueous solution. Even greater difficulties were encountered than in the preceding case, the reaction taking place as slowly, and being less complete; on this account we have not succeeded in preparing the substance in a state of purity, as the following analysis shows; the difference is due to a slight excess of mercuric oxide, which could not be removed, but the result is near enough to leave no doubt about the formula of the compound.

0.3416 gram of substance dried at 100° gave 0.2056 gram of mercuric sulphide.

	Calculated for $[C_6H_3(SO_2NH)_3]_2Hg_3$.	Found.
Mercury	49.02	51.88

Both substances are white powders, insoluble in water, soluble in hydrochloric acid, which form mercuric iodide when boiled with water and iodine for some time; the filtrate, however, contains no organic substance except unaltered benzoltrisulphamide.

The aqueous solution of the amide boiled with plumbic oxide formed white flocks, but the action took place with so much difficulty that we did not try to prepare the substance for analysis. With cupric oxide we could observe no action. A solution of the sulphate of cuprammonium took up the amide with great avidity,

forming a dark blue solution, which deposited azure blue disks of so deep a tint as to look nearly black, while the mother liquor showed only a very pale blue color. The solid was but sparingly soluble in water, being decomposed by it, but tolerably stable in the dry state; dissolved in dilute hydrochloric acid, it gave no precipitate with baric chloride. It was dried in a desiccator, and its composition determined by the following analyses:

I. 0.1628 gram of substance dissolved in hydrochloric acid and precipitated with sodic hydrate gave 0.0356 gram of cupric oxide.

II. 0.2564 gram gave 0.0596 gram of cupric oxide.

	Calculated for $[Cu(NH_3)_4]_3[(SO_3)_3C_6H_3]_2$.	Found. I.	II.
Copper	18.57	17.46	18.57

No better agreement between these results could be expected, when it is remembered that the substance could not be recrystallised. It is evidently cuprammonic benzoltrisulphonate, but we were unable to prepare it by the action of cuprammonic sulphate on a solution of potassic benzoltrisulphonate.

Several attempts to obtain the *imide*, $[C_6H_3(SO_2)_3]_2(NH)_3$, although they led to no definite results, may be mentioned here. The benzoltrisulphochloride mixed with absolutely dry benzol and the silver salt of benzoltrisulphamide, and heated to 100° in a sealed tube for two days, remained entirely unaltered. The experiment could not be repeated at a higher temperature for fear of decomposing the silver salt. If the chloride was heated with the amide, in the proportion of one molecule of each, to 190°, there was no action; but if the temperature was raised to 200°–210°, and maintained at this point for some hours, hydrochloric acid was given off, and a black product formed, which, when treated with cold water, swelled up to a gelatinous mass, the water becoming acid with hydrochloric acid. The jelly thus obtained, after being thoroughly washed with water, dried to a more or less colored powder, insoluble in all the solvents that we have tried, so that we have not been able to purify it properly for analysis. Some nitrogen determinations made with a substance extracted with all the common solvents gave results not far removed from the numbers required by the imide; but they are entitled to little, if any, confidence, as the substance still contained some chlorine. We satisfied ourselves by a special experiment that the substance mentioned above was not formed from the benzoltrisulphamide alone, since

the amide was not altered by heating it to a temperature of 230° for an hour and a half.

Benzoylbenzoltrisulphamide, $C_6H_3(SO_2NHCOC_6H_5)_3$.

Benzoyl chloride has no action on benzoltrisulphamide when the two substances are heated together on the water-bath; if, however, the mixture of these substances in the proportion of three molecules of the chloride to one of the amide (1.3 gram to 1 gram) is heated in a flask with a return cooler to 140° by means of an oil-bath, hydrochloric acid is given off, and the benzoyl derivative is formed. During the process great care must be taken that the temperature does not rise above 150°, as at a point but little above this (150°–180°) decomposition sets in, and in that case the principal product of the action is kyaphenine. After the action has come to an end, which usually takes from five to seven hours, the product is extracted with benzol to remove any undecomposed benzoyl chloride, and purified by crystallisation from hot alcohol. Dried at 100° it gave the following results on analysis:

I. 0.2234 gram of substance gave 13.3 cc. of nitrogen under a pressure of 766 mm. and at a temperature of 22°.

II. 0.1632 gram of substance gave by the method of Carius 0.1784 gram of baric sulphate.

	Calculated for $C_6H_3(SO_2NHC_7H_5O)_3$.	Found. I.	II.
Nitrogen	6.69	6.79	
Sulphur	15.31	...	15.02

Properties. — Benzoylbenzoltrisulphamide crystallises from alcohol in rather short and stout well-formed prisms, with an unmodified basal plane, which seem to belong to the hexagonal system. It has no definite melting point, since it decomposes at comparatively low temperatures (below 200°), and the melting point is therefore modified by the length of time during which the substance has been heated. The highest point which we have observed is 285°, but this can be materially modified by altering the conditions under which the melting point is taken; for instance, two tubes were filled with portions of the same preparation, and one of them was allowed to hang in the bath in the usual way, when it melted at 264°, while the other, which was not allowed to remain in the bath, but only dipped into it occasionally, did not melt till 275°. The two observations were made at the same time,

so that in all other respects the conditions were the same. The melting is accompanied with blackening and effervescence. By long-continued heat at temperatures between 150° and 180° the substance is completely decomposed, giving kyaphenine as the principal product, which was recognised by its melting point, 230° (Pinner and Klein[1] give 231°). The decomposition is undoubtedly similar to that of the corresponding mono compound, which, according to Wallach and Gossmann,[2] gives kyaphenine or benzonitrile and benzolmonosulphonic acid. The benzoyl compound is nearly insoluble in water, whether hot or cold, but not absolutely so, as a moist crystal, after being boiled with water, if laid upon litmus paper, gives an acid reaction. It is tolerably soluble in alcohol or methyl alcohol, especially when boiling, nearly insoluble in ether, chloroform, or glacial acetic acid, essentially insoluble in ligroin, benzol, or carbonic disulphide. It is easily soluble in sodic, ammonic, or baric hydrates, or in sodic carbonate; hydrochloric acid precipitates the original substance from these solutions. The solution in ammonic hydrate, if evaporated to dryness on the water-bath, leaves a colorless varnish, which dissolves again in water; this solution, however, gives no characteristic precipitates with the common reagents, although we may mention the white precipitates produced by argentic nitrate and basic plumbic acetate (neutral plumbic acetate gives no precipitate). We have studied the sodium and barium salts, and intended also to analyse the silver salt, but found that it was too soluble to be purified conveniently by washing, and came down from its hot aqueous solution as a varnish.

Sodic Benzoylbenzoltrisulphamide, $C_6H_3(SO_2NNaC_7H_5O)_3$.—This salt was made by boiling a solution of the calculated amount of sodic carbonate with benzoylbenzoltrisulphamide, and evaporating to dryness, finally spontaneously. Upon drying at 100° it lost varying amounts of water, but in no case so much as one molecule; we are therefore inclined to think it was only hygroscopic water, as the salt was of a varnish-like consistency, which would offer great resistance to air-drying.

0.2466 gram of the salt dried at 100° gave 0.0794 gram of sodic sulphate.

	Calculated for $C_6H_3(SO_2NNaC_7H_5O)_3$.	Found.
Sodium	9.95	10.43

[1] Berichte der deutsch. chem. Gesell. **11**, 764. [2] Ibid. **11**, 754.

The salt is a white varnish, which we did not succeed in obtaining in crystals; it dissolves in water very slowly, but does not need a large amount for complete solution. The solution is neutral, and we did not succeed in preparing an acid salt, as when the free benzoylbenzoltrisulphamide was boiled with one molecule of sodic carbonate, nearly two-thirds of the amide remained undissolved, and the solution was barely acid.

Baric Benzoylbenzoltrisulphamide, $[C_6H_3(SO_2NC_7H_5O)_2]_3Ba_3 12H_2O$.—This salt was made by boiling the benzoylbenzoltrisulphamide with a solution of baric hydrate, and removing the excess of baric hydrate with carbonic dioxide. The solution was evaporated at last spontaneously.

I. 0.3192 gram of the air-dried salt dried at 100° lost 0.0372 gram.

II. 03406 gram at 120° lost 0.0408 gram.

	Calculated for $[C_6H_3(SO_2NC_7H_5O)_2]_3Ba_3 12H_2O$.	Found. I.	II.
Water	11.53	11.65	11.97

The air-dried salt loses in vacuo 3.66 per cent., which corresponds to 3½ molecules of water (calculated 3.36 per cent.).

I. 0.2820 gram of the dry salt gave 0.1184 gram of baric sulphate.

II. 0.2998 gram gave 0.1214 gram of baric sulphate.

	Calculated for $[C_6H_3(SO_2NC_7H_5O)_2]_3Ba_3$.	Found. I.	II.
Barium	24.77	24.69	23.80

It forms a white varnish soluble in water.

Chloride of Benzoylbenzoltrisulphamide, $C_6H_3(SO_2N{=}CCl C_6H_5)_3$.—This substance was made by heating the benzoylbenzoltrisulphamide with phosphoric pentachloride. Equal weights of the two substances were used, and they were heated in an open test tube by means of an air-bath at 110°. After one hour the reaction was complete, and the product was purified by washing it with ligroin, and afterward with absolute ether, which converts it from a viscous liquid to a powder. It was dried at 100° and analysed.

I. 0.2314 gram of substance gave, after boiling with a solution of pure sodic carbonate, 0.1514 gram of argentic chloride.

II. 0.2502 gram of substance gave 0.1614 gram of argentic chloride.

	Calculated for $C_6H_3(SO_2NCCl C_6H_5)_3$.	Found. I.	II.
Chlorine	15.61	16.17	15.95

Properties.—It forms colorless cubic crystals, which, like the benzoyl compound from which they are derived, show no definite melting point; they begin to decompose at 225°, and become liquid in the neighborhood of 245°, but the melting point may vary as much as 30°. The substance is insoluble in water, benzol, ligroin, and chloroform, somewhat soluble in ether.

Benzoltrisulphobenzenylphenylamidine, $C_6H_3[SO_2N=C(NHC_6H_5)C_6H_5]_3$.—The chloride just described was converted by warming it gently with aniline into a viscous mass, which solidified after long standing. The substance was purified by washing with water, ether, and benzol, and then crystallising from hot alcohol until it showed a constant melting point. It was then dried at 100° and analysed.

0.1658 gram of substance gave 14.1 cc. of nitrogen at a pressure of 760 mm. and a temperature of 20°.

	Calculated for $C_6H_3(SO_2N_2C_{13}H_{11})_3$.	Found.
Nitrogen	9.86	9.73

Properties.—It forms white needles, which melt at 196° (uncorr.), and are insoluble in water and ligroin, soluble with difficulty in alcohol, which, however, is the best solvent for it, soluble in ether, benzol, and chloroform.

A number of attempts to make the dibenzoylbenzoltrisulphamide, $C_6H_3[SO_2N(C_7H_5O)_2]_3$, led to no result. The substance was not formed when the sulphamide was heated to 140° with six molecules of benzoyl chloride instead of three, or when the sodium salt of the benzoylbenzoltrisulphamide was heated to 150° for a day with an excess of benzoyl chloride, or when the silver salt of the benzoylbenzolsulphamide (made by adding argentic nitrate to the sodium salt) was heated to 100° in a sealed tube with an excess of benzoyl chloride. In every case the monobenzoylbenzoltrisulphamide remained unaltered.

Benzoltrisulphanilid, $C_6H_3(SO_2NHC_6H_5)_3$.

This substance was prepared by warming benzoltrisulphochloride with aniline. The product was boiled out with water, and purified by crystallisation from alcohol. Dried at 100°, it gave the following result on analysis:

0.2408 gram of the substance gave, according to the method of Carius, 0.315 gram of baric sulphate.

	Calculated for $C_6H_3(SO_2NHC_6H_5)_3$.	Found.
Sulphur	17.68	17.97

Properties.—It forms good-sized short, thick, white prisms, which melt at 237°, and are very slightly soluble in boiling water, soluble in alcohol, ether, benzol, or acetone, but insoluble in ligroin.

Constitution of Benzoltrisulphonic Acid.

We have determined the constitution of the acid in the two following ways.

First Method.—Dry potassic benzoltrisulphonate was mixed thoroughly with exactly the theoretical amount of potassic cyanide (1 gram to 0.45 gram)—if an excess of the cyanide is used, the yield is very much diminished—and heated by means of a gas furnace in a piece of combustion tubing closed at one end; the white crystalline sublimate which collects in the cold part of the tube was removed, and saponified by boiling with alcoholic potassic hydrate, a process which lasts several days. When the evolution of ammonia ceased, the contents of the flask were acidified with hydrochloric acid, and shaken with ether; the ether extract was an acid which melted at 320°–325°, and this melting point remained unaltered after crystallisation from water. It was converted into the silver salt, which gave the following result on analysis:

0.1528 gram of the salt gave on ignition 0.093 gram of metallic silver.

	Calculated for $C_6H_3(CO_2Ag)_3$.	Found.
Silver	61.02	60.86

No other acid could be detected in the product of the reaction. The melting points of the three tribasic acids derived from benzol are, hemimellitic acid, 185°; trimellitic acid, 216°; trimesic acid, above 300°. So there can be no doubt that our acid is *trimesic acid*, and therefore, if there has been no intramolecular transformation, the benzoltrisulphonic acid has the symmetrical constitution 1, 3, 5.

Second Method.—The benzoltrisulphochloride was heated with an excess of phosphoric pentachloride, according to the method of Barbaglia and Kekulé[1] for replacing a sulpho group by an atom of chlorine. For this purpose 3 grams of the chloride were sealed with 5.2 grams of phosphoric pentachloride (one molecule of the sulphochloride to six of the phosphoric pentachloride), and heated for some hours to 200°–210°. Upon treating the product with water, long needles were deposited, which were purified by

[1] Berichte der deutsch. chem. Gesell. **5**, 875.

washing with sodic hydrate and several crystallisations from alcohol, when they melted at 63°. The yield was about 62 per cent. of the theoretical. The melting point of this substance would indicate that it is the symmetrical trichlorbenzol 1, 3, 5, which melts, according to Beilstein and Kurbatow,[1] at 63.5°. To confirm this indication we treated a portion of the substance with fuming nitric acid at a temperature of about 50°, when instead of getting the trichlormononitrobenzol of Beilstein and Kurbatow,[2] melting at 68°, we obtained a substance crystallising in long, thick prisms and melting at 130°. This observation made it necessary for us to study the action of fuming nitric acid on symmetrical trichlorbenzol, the results of which research are described fully in the following paper. It is sufficient to state here that we found the nitric acid used by us, even when acting in the cold, converted the symmetrical trichlorbenzol into the trichlordinitrobenzol, melting at 129.5°, thus proving that the trichlorbenzol derived from benzoltrisulphochloride is the symmetrical compound (1, 3, 5), and confirming the result obtained by the first method.

The study of the action of reducing agents on the benzoltrisulphochloride will be described in a subsequent paper, and Mr. G. T. Hartshorn has undertaken the extension of this method of making sulpho acids to other organic substances, obtaining results which will soon be ready for publication.

LIII.—ON THE ACTION OF NITRIC ACID ON SYMMETRICAL TRICHLORBENZOL.

By C. Loring Jackson and John F. Wing.

We were led to take up the study of this subject by our work upon the constitution of benzoltrisulphonic acid, described in the preceding paper, since the trichlorbenzol derived from that substance by replacing its sulpho groups with chlorine, although melting at 63° like the symmetrical compound (melting point 63.5° according to Beilstein and Kurbatow [3]), gave on treatment with nitric acid a body melting at 130°, whereas Beilstein and Kurbatow obtained in this way trichlormononitrobenzol,[4] melting point 68°.

[1] Annalen der Chemie **192**, 233.
[2] Berichte der deutsch. chem. Gesell. **10**, 271.
[3] Annalen der Chemie **192**, 233.
[4] Berichte der deutsch. chem. Gesell. **10**, 271.

To find the cause of this discrepancy we have prepared the symmetrical trichlorbenzol, and treated it with nitric acid in the cold, when we found that the product was the substance melting at 130° (or more accurately at 129.5°) mentioned above, which proved on analysis to be trichlordinitrobenzol. This result was the more strange, because our nitric acid had a specific gravity of only 1.505, whereas that used by Beilstein and Kurbatow showed 1.52, and in order to get their trichlormononitrobenzol we found it necessary to dilute our acid to 1.46. Since these experiments seemed to show that our nitric acid was more efficient in its action than that used by Beilstein and Kurbatow, we determined to study the subject more carefully, and next attempted the preparation of the trichlortrinitrobenzol, which we obtained without difficulty by boiling the trichlordinitrobenzol for about two hours with a mixture of our nitric acid and fuming sulphuric acid. Both this substance and the dinitro compound are new, the difficulty of the preparation of symmetrical trichlorbenzol having prevented a thorough study of this substance. On the other hand, the corresponding tribrombenzol can be made with great ease, and, as its action with fuming nitric acid has been studied frequently, we decided to extend our experiments to it to see whether in this case also our nitric acid proved more reactive than that of the chemists who have worked in this field heretofore. The complete description of our results with tribrombenzol will be postponed till a later paper, and we shall give here only that portion of them which shows that the action of our nitric acid on tribrombenzol is similar to its action on trichlorbenzol, prefacing it with a brief historical sketch of the work of our predecessors.

Koerner[1] was the first (in 1874) who studied this subject, obtaining on dissolving the symmetrical tribrombenzol with the aid of heat in nitric acid of specific gravity 1.54 the dinitro compound, with a mixture of fuming sulphuric acid and nitric acid the trinitro compound, while all his attempts to obtain the mononitro derivative by direct nitriring failed, owing to the insolubility of the tribrombenzol in weaker acid. In the next year[2] one of us[3] working in the laboratory of Berlin found that the fuming nitric

[1] Gazz. Chim. **4**, 422, 425.

[2] Von Richter (Berichte der deutsch. chem. Gesell. **8**, 1426) succeeded in obtaining the mononitro compound by boiling glacial acetic acid and tribrombenzol with nitric acid of specific gravity 1.52, but found, in agreement with Koerner, that an acid of 1.54 boiled with tribrombenzol converted it into the dinitro compound.

[3] Jackson, Berichte der deutsch. chem. Gesell. **8**, 1172.

acid supplied in that laboratory converted tribrombenzol into the mononitro compound only when boiled with it, and that it was necessary to use a boiling mixture of nitric and (common) sulphuric acids to obtain the dinitro derivative. These observations were confirmed a few years later by Wurster and Beran,[1] who obtained only the mononitro compound from the action of a nitric acid of 1.534 specific gravity alone, and the dinitro compound when its action was reinforced by mixture with crystallised fuming sulphuric acid. Even when this mixture was heated with tribrombenzol in sealed tubes to 220° for 48–60 hours, only a very minute quantity of a trinitro compound was formed; which led them to the conclusion that the trinitro derivative mentioned but not described by Koerner could not be obtained.

In taking up again the study of the nitro compounds of symmetrical tribrombenzol we used the nitric acid of specific gravity 1.505–1.51, which had acted on trichlorbenzol in the way already described, and found that this acid converted the tribrombenzol, even when the mixture was carefully cooled, direct into tribromdinitrobenzol, no mononitro compound being formed; and further, that by the action of a mixture of this nitric acid with fuming sulphuric acid on tribromdinitrobenzol, the tribromtrinitrobenzol, melting point 285°, was formed without difficulty in open vessels. We therefore confirm completely the results of Koerner, so far as they apply to the di and trinitro compounds, in opposition to those obtained by one of us, and by Wurster and Beran; and, to make the comparison more striking, we have used for these experiments tribrombenzol made from some tribromaniline prepared in Berlin by one of us during his previous experiments. To sum up the whole case in a few words, it appears that our nitric acid of specific gravity 1.505–1.51 is much more efficient in its action than the commercial fuming nitric acid used in the laboratories of St. Petersburg[2] (1.52), Berlin,[3] and Munich[4] (1.534); and we are inclined to ascribe the high specific gravities of these commercial acids in part to the presence of lower oxides of nitrogen, while the specific gravity of our acid was due probably exclusively to HNO_3, since it was prepared in our laboratory directly from nitre and sulphuric acid, not pushing the reaction beyond the formation of acid potassic sulphate. This explanation is based upon the observation of Kolb,[5] that the specific gravity of nitric acid is raised by the

[1] Berichte der deutsch. chem. Gesell. **12**, 1821. [2] Beilstein and Kurbatow.
[3] Jackson. [4] Wurster and Beran. [5] Ann. Chim. Phys., ser. 4, **10**, 137.

solution of nitric dioxide in it; and although we cannot submit it to direct experimental proof, since commercial fuming nitric acid is not to be had in this country, yet the following examination of a nitric acid similar to that used in foreign laboratories makes it exceedingly probable that this explanation is correct. This acid was prepared by distilling common nitric acid twice with an excess of sulphuric acid; it had a decided yellow color, and a specific gravity of 1.535 at 15° (the temperature at which all our determinations were made), but converted tribrombenzol into tribrommononitrobenzol only, when acting in the cold, although it gave the dinitro compound when boiled with it. It was therefore less efficient than our acid of specific gravity 1.51, but more so than the foreign acids mentioned above. The analyses of this acid and of our acid of 1.51 specific gravity yielded the following results, which are given in tabular form to facilitate comparison:

	Per Cent. NO_2.	Per Cent. HNO_3.	H_2O by Difference.
Acid of 1.535 sp. gr.	5.0	93.38	1.62
Acid of 1.51 sp. gr.	0.5	96.92 [1]	2.58

The nitric dioxide was determined in the usual way by treatment of the diluted acid with a standard solution of potassic permanganate. The results are not absolutely accurate, as observed by Feldhaus,[2] because of the loss of nitric dioxide in transferring the acid from the weighing or measuring tube to the beaker, but are nearly enough so for our purpose. The nitric acid was determined by neutralisation with ammonic hydrate, and weighing the ammonic nitrate dried at 120°. It contained no ammonic nitrate. The estimated amount of nitric acid corresponding to the nitric dioxide found has been subtracted, so that the number given represents the percentage of free HNO_3 in the acid. These results show that the acid with the higher specific gravity contains the smaller amount of HNO_3, and therefore that the determination of the specific gravity is not a trustworthy way of finding the strength of nitric acid, unless the sample examined is free from lower oxides of nitrogen.

[1] This number is higher than that given by Kolb as corresponding to this specific gravity (1.51), which is 94 per cent. The difference may be due to the presence of amines in the ammonia used by us; but we have not studied this point more carefully, as we are not interested in the absolute determination of the amount of HNO_3 in this acid, but only in the relative amounts of HNO_3 in these two nitric acids, which are given accurately by our numbers, since they were obtained under exactly parallel conditions.

[2] Zeitschrift für anal. Chemie 1, 426.

After the foregoing account of our work was already written we received a paper by Nietzki and Hagenbach,[1] in which a similar experience is described; for they found that with commercial fuming nitric acid a mononitro compound alone could be obtained from diacetylmetaphenylenediamine, whereas they obtained the dinitro compound by using "pure monohydrate," which, they say, can be prepared most easily by distilling fuming nitric acid with twice the quantity of sulphuric acid, and which had a specific gravity of 1.533 at 15°. It is to be observed, however, that our experiment with an acid prepared in a similar way shows that even this acid is not so pure as that made direct from nitre and sulphuric acid.

Preparation of Symmetrical Trichlorbenzol.

We have tried all of the three different processes known for making trichloraniline, viz. 1st. By the direct action of chlorine on aniline dissolved in glacial acetic acid—a method which gives the trichloraniline more quickly than any of the others, but which we discarded on account of the very small yield obtained. 2d. According to Beilstein and Kurbatow,[2] by the formation of chloracetanilid from chlorine and acetanilid, and converting this, after the removal of the acetyl, into trichloraniline by treatment with chlorine in a glacial acetic acid solution. We may be allowed to remark, in regard to this method, that we were unable to make acetanilid in glacial acetic acid solution take up more than one atom of chlorine, an excess of chlorine passing through the solution unaltered after monochloracetanilid had been formed, whereas Beilstein and Kurbatow obtained the dichloracetanilid in this way; we have not thought the point of sufficient importance, however, to devote to it the time necessary to determine the cause of this difference. This method gives good results, but does not lead to them so quickly and easily as the *third*, which consists in making dichloracetanilid according to Witt,[3] that is, acting on acetanilid in a warm acetic acid solution with a solution of bleaching-powder. The dichloracetanilid was then converted into the trichloraniline, as in the second method.

The method, therefore, which we finally adopted, and should recommend as the best, is the following: 5 parts of acetanilid are

[1] Berichte der deutsch. chem. Gesell. **20**, 333. [2] Annalen der Chemie **182**, 95.

[3] Berichte der deutsch. chem. Gesell. **8**, 1226. Bender, ibid. **19**, 2272, has obtained $C_6H_3NClCOCH_3$ by the action of bleaching-powder on a *cold* acetic acid solution of acetanilid.

dissolved in 20 parts of glacial acetic acid and 100 of water, and heated to boiling; then, after removing the lamp, a 10 per cent. solution of bleaching-powder is added, until a viscous precipitate is formed, the temperature being kept above 70°. The precipitate is then treated with ammonic hydrate, and crystallised from alcohol. The yield of dichloracetanilid is nearly quantitative. The dichloracetanilid is next converted into dichloraniline by heating it on the water-bath with strong sulphuric acid, the dichloraniline dissolved in glacial acetic acid, and chlorine passed through the solution until two parts of the dichloraniline have gained one part of chlorine; the product is then rendered alkaline with a large excess of sodic hydrate, and distilled with steam; the solid which distills over, after crystallisation from dilute alcohol, is pure trichloraniline, but the yield is far from satisfactory, a large quantity of tarry impurity being formed during the treatment of the free base with chlorine. The trichloraniline is converted into trichlorbenzol by the method of Bässmann;[1] that is, it is dissolved in alcohol of 95 per cent. by heat, and the calculated amount of a hot concentrated aqueous solution of potassic nitrite added, and then dilute sulphuric acid, little by little, until the reaction is strongly acid; the mixture is then warmed gently on the water-bath until the reaction comes to an end, and the trichlorbenzol purified by crystallisation from alcohol. The yield is good, 8 grams of the trichloraniline giving 5 grams of trichlorbenzol; that is, 67 per cent. of the theoretical amount.

Trichlordinitrobenzol, $C_6HCl_3(NO_2)_2$.

The symmetrical trichlorbenzol was dissolved in nitric acid[2] of specific gravity 1.505 at the ordinary temperature; the same result was also obtained if the beaker in which the reaction took place was kept cool by immersion in cold water. When the trichlorbenzol was completely dissolved, the product was precipitated by pouring it into cold water or snow, and purified by crystallisation from hot alcohol until it showed the constant melting point 129.5°, when it was dried at 100° and analysed.

0.2694 gram of the substance gave 24.4 cc. of nitrogen at 24° temperature and 766.5 mm. pressure.

[1] Annalen der Chemie **191**, 206.

[2] The nitric acid was prepared by distilling nitre with sulphuric acid in the proportions of one molecule of each. See page 350 for a discussion of this point.

0.2102 gram of substance gave, according to the method of Carius, 0.3322 gram of argentic chloride.

	Calculated for $C_6HCl_2(NO_2)_2$.	Found.
Nitrogen	10.31	10.24
Chlorine	39.22	39.07

Properties.—It forms thick, long white prisms, when crystallised from alcohol, which melt at 129.5°, and are soluble in cold alcohol, much more freely in hot, very easily soluble in benzol, chloroform, carbonic disulphide, or acetone, soluble in ether, or in glacial acetic acid, still more soluble in hot glacial acetic acid.

In order to obtain trichlormononitrobenzol, a nitric acid diluted until it shows the specific gravity 1.46 must be boiled with trichlorbenzol until complete solution takes place. After precipitation with water and recrystallisation from alcohol, the product of such a preparation showed the melting point 68°, that given by Beilstein and Kurbatow. Ordinary strong nitric acid of specific gravity 1.4 has no action on trichlorbenzol, whether hot or cold.

The constitution of the trichlordinitrobenzol follows from the fact that it is made from symmetrical trichlorbenzol, and is

$$H : Cl : NO_2 : Cl : NO_2 : Cl = 1 : 2 : 3 : 4 : 5 : 6.$$

Trichlortrinitrobenzol, $C_6Cl_3(NO_2)_3$.

This substance was made by boiling in a flask, for half an hour or somewhat more, trichlordinitrobenzol with a mixture of fuming sulphuric acid and nitric acid of specific gravity 1.505, prepared direct from nitre and sulphuric acid.[1] The substance goes completely into solution while hot, but a considerable quantity separates out as it cools. The whole is then precipitated with snow, and treated with hot alcohol, when an insoluble residue containing sulphur is left behind; this is probably a sulphone, but was formed in such small quantities that we did not try to study it. The hot alcoholic solution on cooling deposits the trichlortrinitrobenzol, which is purified by crystallisation from boiling alcohol until it shows a constant melting point 187°. The substance was dried at 100° and analysed, with the following results:

0.1656 gram of substance gave 18.8 cc. of nitrogen at a temperature of 18° and 750 mm. pressure.

[1] See page 350.

0.1486 gram of substance gave, according to the method of Carius, 0.2034 gram of argentic chloride.

	Calculated for $C_6Cl_3(NO_2)_3$.	Found.
Nitrogen	13.27	12.94
Chlorine	33.64	33.83

Properties.—The trichlortrinitrobenzol is obtained by crystallisation from alcohol in rather thick good-sized needles of a white color, with a slight yellowish tinge, melting point 187°, very nearly insoluble in water, but not completely so, less soluble in alcohol than trichlordinitrobenzol, easily soluble in ether, benzol, chloroform, acetone, glacial acetic acid, or carbonic disulphide. Alcohol is the best solvent for it.

The constitution of the trichlortrinitrobenzol, since it is made from the symmetrical trichlorbenzol, is also symmetrical,

$$Cl : NO_2 : Cl : NO_2 : Cl : NO_2 = 1 : 2 : 3 : 4 : 5 : 6.$$

The description of the tribromtrinitrobenzol, as well as of some of the derivatives of this very reactive substance, will be postponed until another paper.

Contributions from the Sheffield Laboratory of Yale University.

XXIX.—ON NITRO DERIVATIVES OF OXANILIDE.

By W. G. Mixter and F. O. Walther.

Paradinitro-oxanilide.—Huebner and Rudolph[1] prepared dinitro-oxanilide by adding fuming nitric acid to a solution of oxanilide in glacial acetic acid. We have obtained the compound by treating 10 grams of oxanilide with 150 cc. of nitric acid, sp. gr. 1.4, and warming on a water-bath. The oxanilide did not dissolve, but changed to a thick pasty mass. The product was washed with water and dried at 100°. It weighed 12 grams, the theoretical yield being 13.7 grams. An estimation of nitrogen gave 17.13 per cent.; theory requires 16.97 per cent. in dinitro-oxanilide. The preparation was found to have the melting point 260°, and to yield on saponification p-nitraniline, as described by Huebner and Rudolph. The p-nitraniline obtained was found to be free from o-nitraniline.

[1] Berichte der deutsch. chem. Gesell. 8, 473.

Tetranitro-oxanilide.—When oxanilide is slowly added to red fuming nitric acid it dissolves, and after a few minutes small crystals appear. On warming, crystals form abundantly. To complete the reaction we usually boiled the solution ten to fifteen minutes. After cooling, the crystalline mass was filtered on a perforated platinum cone, washed two or three times with nitric acid, sp. gr. 1.4, then with water and, finally, once with alcohol, and dried at 100°. 10 grams of oxanilide yielded 11 grams, and sometimes a little more, of crystals of tetranitro-oxanilide. The acid filtrate from the crystals, on diluting with water, gave a precipitate of tetranitro-oxanilide, rather less than half the weight of the crystalline portion and not quite as pure. The following analyses are of two different preparations:

I. 0.5297 gram gave 0.7711 gram CO_2 and 0.0981 gram H_2O. 0.4247 gram gave 72.75 cc. N at 21° and 768.4 mm.

II. 0.4982 gram gave 0.7211 gram CO_2 and 0.0854 gram H_2O. 0.4406 gram gave 74.2 cc. N at 14° and 759 mm.

	Theory.	I.	II.
C_{14}	40.00	39.69	39.92
H_8	1.90	2.06	1.91
N_8	20.00	20.20	20.12
O_{10}	38.10	...	...
	100.00		

Tetranitro-oxanilide has a white color, melts at 300°, is but slightly soluble in hot alcohol and benzene and glacial acetic acid. It is readily saponified by a hot two per cent. potassium hydroxide solution, by warm oil of vitriol, and by an alcoholic ammonia solution at 100°, yielding 1:2:4 dinitroaniline, melting at 182°.

It has, therefore, the constitution represented by

$$\begin{array}{l} \overset{1}{\text{CO}}\text{NHC}_6\text{H}_3\overset{2}{\text{NO}_2}\overset{4}{\text{NO}_2} \\ | \\ \underset{1}{\text{CO}}\text{NHC}_6\text{H}_3\underset{2}{\text{NO}_2}\underset{4}{\text{NO}_2}. \end{array}$$

Hexnitro-oxanilide.—Oxanilide, 10 grams, was dissolved in 150 cc. of red fuming nitric acid at ordinary temperature, and oil of vitriol, 150 cc., was added. A bulky precipitate, consisting of minute pearly scales, at once separated. After warming for half an hour on a water-bath the mixture was cooled, poured into cold water, and the precipitate was filtered and thoroughly washed with

water. The product, dried at 100°, weighed 19.3 grams. It is designated as A. Another preparation, B, was made as above described, only in place of oil of vitriol, warm fuming sulphuric acid was used, and the acid mass was poured into snow. The yield was 20.7 grams. Another time the fuming sulphuric acid was heated to 100° before adding it to the nitric acid solution, and no higher nitro compound was obtained. The yield was less than in the preparations A and B.

Analysis of A.—0.4272 gram gave 0.5225 gram CO_2 and 0.0506 gram H_2O.

0.3789 gram gave 64.7 cc. N at 4° and 768.7 mm.

Analysis of B.—0.5794 gram gave 0.700 gram CO_2 and 0.0662 gram H_2O.

0.3700 gram gave 67.6 cc. N at 13° and 765.5 mm.

	Theory.	A.	B.
C_{14}	32.94	33.33	32.95
H_6	1.18	1.32	1.23
N_8	21.96	21.38	22.03
O_{14}	43.92	...	...
	100.00		

Hexnitro-oxanilide melts at 300°, has a white pearly lustre, is slightly soluble in boiling alcohol and benzene, and is somewhat more soluble in hot glacial acetic acid.

It does not dissolve in oil of vitriol at 100°, but complete solution results on raising the temperature to 200°, and trinitraniline is formed. That which we obtained after recrystallising once from alcohol melted at 188°, the melting point of the only trinitraniline known in which $NH_2 : NO_2 : NO_2 : NO_2 = 1 : 2 : 4 : 6$.

An estimation of nitrogen gave 24.73 per cent.; theory requires 24.56 per cent. in $C_6H_2(NO_2)_2NH_2$. The hexnitro-oxanilide therefore has the formula

$$\begin{array}{l} \overset{1}{C}ONHC_6H_2\overset{2}{N}O_2\overset{4}{N}O_2\overset{6}{N}O_2 \\ | \\ CONHC_6H_2NO_2NO_2NO_2. \\ \underset{1}{} \quad \underset{2}{} \quad \underset{4}{} \quad \underset{6}{} \end{array}$$

Hexnitro-oxanilide differs from the other oxanilides in its deportment towards alkalies. It dissolves quickly in hot alkaline solutions, forming a deep red solution of two or more compounds. In one experiment 2 grams of hexnitro-oxanilide were treated with

5 grams of potassium hydroxide in 100 cc. of water. The solution was boiled for two hours; ammonia was given off. To the solution acetic acid was added in excess, and the small black precipitate which formed was filtered and dissolved in hot water. Nothing separated on cooling this last solution. We then tried the action of ammonia as follows: 5 grams of hexnitro-oxanilide were placed in a litre of boiling water containing a little ammonia; the red solution was filtered from a yellow insoluble part, doubtless trinitraniline. The solution on cooling yielded brilliant small crystals of a red color, showing also golden tints. Two different preparations of these crystals dried at 100° gave the following results on analysis:

Carbon	32.18	32.53
Hydrogen	2.41	2.39
Nitrogen	24.92	24.87

These figures do not correspond to any simple atomic ratio and we do not understand what compounds composed the mixture, except that subsequent results indicate that an ammonium salt of trinitrophenyloxamide was present. The red crystals were next dissolved in water, and acetic acid in one case, and hydrochloric acid in another, added. A light yellow precipitate slowly separated on boiling, which was washed, dried, and gave analytical results which indicated a mixture. In another experiment 10 grams of hexnitro-oxanilide were treated with a litre of boiling water containing 100 cc. of concentrated ammonia. The insoluble portion was found to be trinitraniline. The filtered solution was acidified with hydrochloric acid. The red color slowly disappeared. The precipitate was washed with *cold* water and dissolved in boiling glacial acetic acid. The solution on cooling changed to a jelly. The acetic acid was removed by repeated evaporations with alcohol, and finally a fibrous mass was obtained, which was washed with alcohol and dried. It is designated as A. Next 10 grams of hexnitro-oxanilide were placed in 300 cc. of boiling water in which 30 grams of hydrogen potassium carbonate had been dissolved; carbon dioxide was set free by the anilide, and the escaping steam gave a faint reaction for ammonia. Only a small residue remained undissolved. The solution on slow cooling deposited red crystals of a potassium salt, or salts in appearance like those obtained with ammonia. They were filtered and washed

moderately with *cold* water. The filtrate from the crystals was acidified, the slight precipitate which formed was removed, and this solution was evaporated to dryness. The residue was treated with cold water, the solution filtered, made acid with acetic acid, and calcium chloride added. The calcium salt obtained was analysed and found to be oxalate, thus proving that oxalic acid is one of the products of the decomposition of hexnitro-oxanilide by potassium carbonate. The red crystals of the potassium salt above mentioned were placed in about 250 cc. of water, and acetic acid in large excess was added. The whole was boiled until the red color disappeared, and the yellow product was filtered and washed with *cold* water. The product was treated with about 800 cc. of boiling alcohol, which dissolved most of it. The alcoholic solution on cooling and evaporating spontaneously yielded a fibrous mass, which was filtered, washed with cold alcohol, and dried at 100°. It weighed 2.3 grams, and is designated as B.

In the next experiment 27 grams of hexnitro-oxanilide and an equal weight of hydrogen potassium carbonate and about 800 cc. of water were used. The insoluble portion which remained on boiling was removed; it proved to be trinitraniline. The potassium salt which separated on cooling the solution was filtered, the filtrate was made acid with acetic acid, heated to boiling, and the slight precipitate which formed was removed. This solution on cooling deposited potassium picrate, from which picric acid was obtained, as was proved by its melting point, 122°, and its reactions with potassium cyanide and with ammoniacal copper sulphate. The potassium salt obtained, not the picrate, was dissolved in hot water and decomposed by acetic acid. The precipitate was treated several times with hot water, but only for a short time. It is designated as C.

Analysis of A.—0.4644 gram gave 0.5456 gram CO_2 and 0.0753 gram H_2O.

0.4251 gram gave 84.6 cc. N at 11° and 742 mm.

Analysis of B.—0.4723 gram gave 0.5557 gram CO_2 and 0.0753 gram H_2O.

0.4126 gram gave 77.14 cc. N at 4.7° and 768 mm.

Analysis of C.—0.502 gram gave 0.5866 gram CO_2 and 0.0787 gram H_2O.

0.4474 gram gave 84.2 cc. N at 9° and 763 mm.

	Calculated for	A.	B.	C.
C_8	32.11	32.04	32.09	31.69
H_5	1.67	1.78	1.77	1.74
N_5	23 41	23.46	23.33	22.98
O_8	42.81	...	...	...
	100.00			

The results show that the substance purified by three different methods has the formula $C_8H_5N_5O_8$.

The substance was warmed with sulphuric acid, and in the escaping gases carbon monoxide and dioxide were identified, and from the acid solution trinitraniline was separated. The potassium salt, described later, was found to decompose slowly when its aqueous solution was boiled, with formation of trinitraniline and oxalic acid. These reactions indicate that the substance is trinitrophenyl-oxamide, having the formula

$$\begin{array}{l} CONHC_6H_2(NO_2)_3 \\ | \\ CONH_2. \end{array}$$

Trinitrophenyl-oxamide melts with decomposition at 255°–260°. It is slightly soluble in alcohol, but dissolves readily in hot glacial acetic acid, from which it separates on cooling in white fibres. Its potassium salt, made in and crystallised from hot alcohol, was found to contain 11.64 per cent. of potassium; theory requires 11.57 per cent. in $C_8H_4N_5O_8K$. A preparation of potassium salt which was crystallised from hot water yielded only 10.31 per cent. of potassium, and in crystals obtained from hexnitro-oxanilide and potassium carbonate only 9.96 per cent. of potassium was found. These two results are due to the decomposition already mentioned of the potassium salt. Trinitrophenyl-oxamide forms compounds with zinc, calcium, barium, and silver, which have not been analysed. The ammonium salt forms brilliant yellowish-red thin crystals, like the potassium salt in appearance. Both explode violently on heating. The strong acidic character of trinitrophenyl-oxamide is indicated by the fact that solutions of its ammonium and potassium compounds are not decomposed, or only partly, by hydrochloric and acetic acids at ordinary temperature.

The decomposition of hexnitro-oxanilide by potassium carbonate or ammonia is evidently as follows:

$$\begin{array}{l}\mathrm{CONHC_6H_3(NO_2)_2}\\ |\\ \mathrm{CONHC_6H_3(NO_2)_2}\end{array} + \mathrm{H_2O} = \begin{array}{l}\mathrm{CONHC_6H_3(NO_2)_2}\\ |\\ \mathrm{CONH_2}\end{array} + \mathrm{C_6H_3(NO_2)_2OH}.$$

At the same time the trinitrophenyl-oxamide is partly converted into trinitraniline and oxalic acid, thus:

$$\begin{array}{l}\mathrm{CONHC_6H_2(NO_2)_3}\\ |\\ \mathrm{CONH_2}\end{array} + 2\mathrm{H_2O} = \mathrm{C_6H_2(NO_2)_3NH_2} + \begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array} + \mathrm{NH_3}.$$

Water is represented as taking part in the reactions to avoid formulating the compound of trinitrophenyl-oxamide with potassium, whose constitution has not been determined. It should be stated that di- and tetranitro-oxanilide do not yield analogues of trinitrophenyl-oxamide, and that from none of the nitro-oxanilides have oxanilic acids been obtained.

XXX.—ON NITRO DERIVATIVES OF DIBROMOXANILIDE.

By W. G. Mixter and C. P. Willcox.

Dinitrodibrom-oxanilide.—Paradibrom-oxanilide, 5 grams, and nitric acid, sp. gr. 1.4, 150 cc., were boiled gently for half an hour. The dibromoxanilide only partly dissolved. After cooling, the whole was poured into cold water, and the insoluble portion was filtered, washed thoroughly with water and once with alcohol, and dried at 100°. The following is the analysis:

I. 0.5252 gram gave 0.676 gram CO_2 and 0.0823 gram H_2O.
II. 0.7495 gram gave 0.959 gram CO_2 and 0.1173 gram H_2O.
III. 0.3128 gram gave 0.4013 gram CO_2.
IV. 0.4337 gram gave 41 cc. N at 4° and 748.8 mm.
V. 0.4088 gram gave 0.3147 gram AgBr.

	Theory.	I.	II.	III.	IV.	V.
C_{14}	34.42	35.09	34.89	34.98	...	...
H_8	1.64	1.74	1.74	...	...	...
N_4	11.47	...	...	...	11.53	...
Br_2	32.79	...	...	...	...	32.75
O_6	19.68	...	...	...	...	...
	100.00					

Dinitrodibrom-oxanilide has a yellow color, melts at 285° to 288°, is insoluble in boiling alcohol and benzene, and is soluble in hot aniline. It was saponified by potassium hydroxide solution, and the nitrobromaniline obtained melted at 107°. Another portion was saponified with warm oil of vitriol, and the resulting nitrobromaniline after recrystallising from hot water melted at 110°.

The melting point of o-nitro-p-bromaniline is 111.4°, hence the dinitrodibrom-oxanilide has the formula

$$\begin{matrix} {}^{1}\mathrm{CO}{}^{2}\mathrm{NHC_6H_3NO_2}{}^{4}\mathrm{Br} \\ | \\ \underset{1}{\mathrm{CO}}\mathrm{NHC_6H_3}\underset{2}{\mathrm{NO_2}}\underset{4}{\mathrm{Br}}. \end{matrix}$$

It should be mentioned that in one experiment we failed to obtain nitration of all the bromoxanilide, but from the mixture prepared o-nitro-p-bromaniline.

Tetranitrodibrom-oxanilide.—In attempting to introduce more than two nitro groups into dibromoxanilide we have found it difficult to obtain pure products. In one experiment 5 grams of dibromoxanilide were added gradually to 150 cc. of fuming nitric acid. The mixture was stirred frequently, and after half an hour was poured into snow. The substance was analysed, but a formula could not be deduced from the results. In another trial dibrom-oxanilide was added to fuming nitric acid, cooled by a freezing mixture, and the nitrogen found in the product was only 12.9 per cent. When dibromoxanilide is dissolved in warm red fuming nitric acid, bromine is set free. The solution, when concentrated by boiling, deposits crystals. We used 20 cc. of fuming acid for every gram of dibromoxanilide taken. The crystals were washed first with nitric acid of 1.4 sp. gr. and then with water, and analysed with the following results:

I. 0.3368 gram gave 0.3552 gram CO_2 and 0.0331 gram H_2O.
II. 0.2470 gram gave 0.2623 gram CO_2 and 0.0253 gram H_2O.
III. 0.5555 gram gave 65.56 cc. N at 7.6° and 768.1 mm.
IV. 0.3545 gram gave 41.21 cc. N at 4.7° and 772.3 mm.
V. 0.6016 gram gave 0.392 gram AgBr.

The theory given is for $\begin{matrix} \mathrm{CONHC_6H_2(NO_2)_2Br} \\ | \\ \mathrm{CONHC_6H_2(NO_2)_2Br}. \end{matrix}$

	Theory.	I.	II.	III.	IV.	V.
C_{14}	29.06	28.76	28.96	...	...	...
H_6	1.04	1.09	1.13	...	...	...
N_8	14.53	...	...	14.58	14.59	...
Br_2	27.68	...	...	...	...	27.72
O_{10}	27.69	...	...	...	...	...

Tetranitrodibrom-oxanilide forms white needles which melt at 285°–287°. It is almost insoluble in boiling alcohol, and is sparingly soluble in boiling glacial acetic acid, from which it separates on cooling in white fibres. We have not succeeded in obtaining dinitrobromaniline by saponifying the substance with sulphuric acid, in which it dissolves on heating, or with potassium hydroxide.

As hexnitro-oxanilide behaves differently from other oxanilides when treated with alkalies (see preceding article), we have endeavored to obtain a similar decomposition of tetranitrodibrom-oxanilide, but as yet have no results, owing to lack of material and time. Its solution in hot alcoholic ammonia deposited on cooling a yellow mass, which, after drying, melted at 285°. The tetranitrodibrom-oxanilide was found to dissolve in hot aqueous alcohol containing potassium carbonate. Nothing separated from the solution on cooling.

The filtrate from the crystals of tetranitrodibrom-oxanilide which separated from nitric acid in the preparation, yielded a nearly white precipitate on diluting with water. It was washed with water and dried at 100°. It is designated as A, and another preparation obtained in the same way as B.

Analysis of A.—I. 0.4045 gram gave 0.4958 gram CO_2 and 0.0538 gram H_2O.

II. 0.3945 gram gave 55.2 cc. N at 8.2° and 739.4 mm.

III. 0.2407 gram gave 0.0993 gram AgBr.

Analysis of B.—IV. 0.4256 gram gave 0.515 gram CO_2 and 0.0578 gram H_2O.

V. 0.4095 gram gave 53.12 cc. N at 4° and 772 mm.

VI. 0.4522 gram gave 0.191 gram AgBr.

	Theory.	I.	II.	III.	IV.	V.	VI.
C_{12}	33.64	33.42	...	...	33.00	...	...
H_6	1.40	1.48	...	...	1.48	...	...
N_8	16.35	...	16.59	...	...	16.25	...
Br	18.69	...	...	17.55	...	...	18.49
O_8	29.92	...	...	...	...	...	...
	100.00						

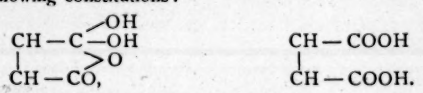
The results correspond fairly well with the calculated formula. The constitution of the substance has not been made out. It is soluble in dilute ammonia, and the solution yields a barium salt on addition of a solution of barium chloride.

REMARKS ON THE CONSTITUTION OF LEVULINIC AND MALEIC ACIDS.

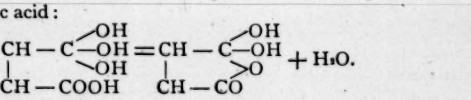
By Arthur Michael.

Several years ago, W. Roser[1] attempted to explain the isomerism of maleic and fumaric acids by assuming the first-named substance to be an anhydride of a hypothetical orthomaleic acid. At the time of its publication this view was without an experimental basis; but R. Anschütz,[2] in recently reviving it, has endeavored to prove that subsequent discoveries have given this hypothesis the needed experimental support. The constitution of maleic and fumaric acids is one of the most important problems of organic chemistry, and I therefore deemed an examination of Roser's hypothesis of interest, particularly as Anschütz's paper may seem to establish this view with some certainty.

According to Roser, maleic and fumaric acids are expressed by the following constitutions:



Maleic acid is therefore the anhydride of an acetyleneorthodicarboxylic acid:



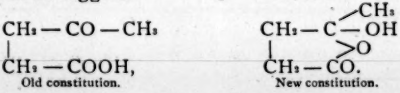
This conception of the constitution of maleic acid rests on two assumptions, which are, that the acid contains a typical carbon with a strong affinity for two hydroxyls, and that carboxyl and ortho-

[1] Berichte der deutsch. chem. Gesell. **14**, 2546.

[2] This Journal **9**, 253; Annalen der Chemie **239**, 161.

carboxyl in the γ-position are unstable, and undergo a spontaneous decomposition under elimination of water. Anschütz explains the first assumption by calling attention to the existence of chloral-hydrate, mesoxalic and dioxytartaric acids, which compounds, like Roser's constitution of maleic acid, contain a carbon that is in union with strong negative groups. Acetic aldehyde does not form a hydrate with water, but the replacement of the methyl-hydrogen by halogen gives rise to compounds possessing that property. It evidently follows that the replacement of hydrocarbon-hydrogen in maleic and similar acids by halogens should strengthen the affinity of the two hydroxyls to the typical carbon, and the halogen acids should therefore be more stable towards heat than the original compounds. It is worthy of note, however, that the introduction of halogen has exactly the contrary effect. While maleic and citraconic acids are perfectly stable even at 100°, dibrommaleic and monobromcitraconic acids decompose, more or less completely, at ordinary temperature into anhydrides and water.

In considering the facts adduced by Anschütz in support of Roser's maleic acid constitution, their order, as given in his paper, will be followed. One of Anschütz's principal proofs is found in the discovery of Bredt,[1] that levulinic acid heated with acetic anhydride gives an acetyl derivative. Although Bredt states that this fact is not in accordance with the generally adopted constitution of the acid, he also calls attention to the behavior of the acid towards hydroxylamine, phenylhydrazine, and hydrocyanic acid, as proving the presence of carbonyl in levulinic acid, and that these reactions are in harmony with the old constitution and not with the one he suggests:



Old constitution. New constitution.

Anschütz, however, believes that the formation of an acetyl derivative proves the new constitution beyond a doubt, and changes the constitutions of a number of analogous substances in a corresponding manner. Accordingly, the constitution of trichlor-phenomalic acid is changed to contain an anhydro-oxygen, and its conversion by barium hydrate into maleic acid is considered as proving Roser's view in regard to the constitution of that acid:

[1] Annalen der Chemie **236**, 225.

$$\begin{array}{l} CH-CH\overset{CCl_3}{\underset{}{<}}O \\ |\qquad\quad > OH \\ CH-CO \end{array} + Ba(OH)_2 = \begin{array}{l} CH-C\overset{O}{\underset{O}{<}}>Ba \\ |\qquad\quad > O \\ CH-CO \end{array} + CHCl_3 + H_2O.$$

It seems to me that the formation of the so-called acetyl-levulinic acid is a result of the relative positions of carbonyl and carboxyl in the old constitution of the acid, and that, when this relation is duly considered, it will be found that the formation of the acetyl compound is simply what should be expected.

It is a well-known fact that aldehydes unite with acid anhydrides and chlorides to form ethers. Although, to my knowledge, this reaction has not been realised with ketones, no one bearing the close similarity in the reactions of aldehydes and ketones in mind can well doubt that ketones are capable of forming similar compounds. We may therefore suppose that the first phase in the action of acetic anhydride on levulinic acid is to form a diacetyl product:

$$\begin{array}{l} CH_3-CO-CH_2 \\ |\qquad\quad \\ CH_2-COOH \end{array} + (CH_3CO)_2O = \begin{array}{l} CH_3-C(O-OCCH_3)_2-CH_3 \\ | \\ CH_2-COOH. \end{array}$$

This compound is the acetyl derivative of a γ-dihydroxyvaleric acid, and we know that hydroxyl and, probably still more readily, the group $-O-OCCH_3$ in the γ- and δ-positions to carboxyl, have a tendency to undergo a condensation.[1] The second phase of the reaction therefore consists in the elimination of acetic acid, and is represented as follows:

$$\begin{array}{l} CH_3-C\overset{O-OCCH_3}{\underset{O-OCCH_3}{<}}-CH_2 \\ |\qquad\qquad\quad \\ CH_2-COOH \end{array} = \begin{array}{l} CH_3-C-(O-OCCH_3)-CH_2 \\ |\qquad\quad > O \\ CH_2-CO \end{array} + CH_3COOH.$$

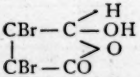
It will be noticed that the constitution of the acetyl derivative is identical, no matter which of the two structural formulæ of levulinic acid is used, and that the new interpretation of its formation is in complete accordance with the old carbonyl-constitution of the acid. While the old constitution explains in a satisfactory manner the formation of levulinic acid from acetylsuccinic ether and all its reactions, the new constitution suggested by Bredt, and adopted by Anschütz, cannot be brought in harmony with that synthesis

[1] Tiemann and Herzfeld (Berichte der deutsch. chem. Gesell. **10**. 287) have shown that coumarine is readily formed when acetylcoumaric acid is heated, but cannot be obtained by heating coumaric acid.

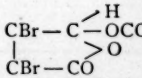
nor with its principal reactions. I do not hesitate to assert that the old constitution of levulinic acid has been established with a certainty that is uncommon among carbon derivatives of the higher series. If, as Anschütz[1] asserts, Kekulé and Strecker[2] have proved that trichlorphenomalic acid is an "unsaturated levulinic acid in which the hydrogen of the methyl has been replaced by chlorine," then it is evident that its decomposition by barium hydrate into maleic acid and chloroform speaks with as much force against Roser's constitution as Anschütz supposed the reaction to speak in its favor:

$$\begin{array}{l} CH{-}CO{-}CCl_3 \\ | \\ CH{-}COOH \end{array} + Ba(OH)_2 = \begin{array}{l} CH{-}COO \\ | \\ CH{-}COO \end{array} > Ba + CHCl_3 + H_2O$$

The explanation of the formation of acetyl-levulinic acid given above applies equally to that of the so-called acetylmucobromic acid. Jackson and Hill[3] have shown that mucobromic acid and acetyl chloride heated at 120° give an acetyl derivative, and Anschütz considers its formation as proving the following constitutions:



Mucobromic Acid.



Acetylmucobromic Acid.

From the new point of view, the formation of the so-called acetylmucobromic acid is a result of the property of aldehydes to unite with acid chlorides, and the presence of a reactive chlorine, due to the juxtaposition of the negative group $OCOCH_3$, in the γ-position towards carboxyl:

$$\begin{array}{l} CBr{-}CHO \\ | \\ CBr{-}COOH \end{array} + CH_3COCl = \begin{array}{l} CBr{-}C(H){-}OCOCH_3 \\ | \quad\quad\quad\; \backslash Cl \\ CBr{-}COOH \end{array}$$

$$\begin{array}{l} CBr{-}C(H){-}OCOCH_3 \\ | \quad\quad\quad\; \backslash Cl \\ CBr{-}COOH \end{array} = \begin{array}{l} CBr{-}C(H){-}OCOCH_3 \\ | \quad\quad\quad\; > O \\ CBr{-}CO \end{array} + HCl$$

The anil of maleic acid treated with alkalies gives a salt of fumaric acid and aniline. This interesting fact has been used by Anschütz to corroborate Roser's hypothesis of the constitution of

[1] This Journal **9**, 263; Annalen der Chemie **239**, 176. [2] Ibid. **223**, 170.
[3] This Journal **3**, 42.

maleic acid. According to this interpretation, the anil assimilates water to pass over into the acid anilide of fumaric acid, a reaction that Anschütz represents as follows:

$$\begin{matrix} CH-CO \\ | \quad > NC_6H_5 \\ CH-CO \end{matrix} + H_2O = \begin{matrix} CH-CONHC_6H_5 \\ | \\ CH-COOH. \end{matrix}$$

It has already been stated that Roser's hypothesis necessitates assuming a carbonyl in maleic anhydride with a strong affinity for water, and a typical carbon in the acid with an affinity for two hydroxyls. If the so-called anil of maleic acid is, as Anschütz supposes, a derivative of maleic acid, it should behave towards alkalies exactly as maleic anhydride does; that is, its carbonyl should assimilate water to form an acid anilide of maleic acid:

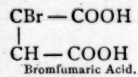
$$\begin{matrix} CH-CO \\ | \quad > NC_6H_5 \\ CH-CO \end{matrix} + H_2O = \begin{matrix} CH-CONHC_6H_5 \\ | \\ CH-COOH. \end{matrix}$$

When experiments show, however, that the acid anilide of fumaric acid is the compound formed in this reaction, we are forced to the conclusion that the affinity of carbonyl for water, which is so characteristic for maleic anhydride, has been lessened by the replacement of oxygen by NC_6H_5, although that radical is obviously of a pronounced negative character. If we accept this second, in itself improbable, assumption, it is evident that the change from a maleic to a fumaric derivative consisted not in the mere mechanical rearrangement of formulæ as represented by Anschütz, but in the replacement of oxygen by NC_6H_5; hence the so-called maleinanil is, properly speaking, the anil of fumaric acid, and its decomposition into that acid is simply what might be expected. But the assumption that the replacement of an oxygen in maleic anhydride by NC_6H_5 lessens the affinity of carbonyl for water is directly contradicted by the behavior of citraconanil with alkalies. According to Gottlieb,[1] citraconanil, or methylmaleinanil, heated for a short time with dilute ammonia gave ammonium citraconate and aniline. As the replacement of hydrocarbon-hydrogen by alkyl in the acids of the maleic series increases the tendency of these compounds to form anhydrides, or, in other words, lessens the affinity of the typical carbon for hydroxyl, we should expect, if the second assumption is valid, that the replacement of an oxygen in citraconic or methylmaleic anhydride by

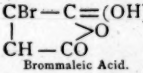
[1] Annalen der Chemie 77, 28.

NC_6H_5 would give, even more readily than the corresponding change in maleic anhydride gives fumaranil, mesacon-, or methylfumaranil. The formation of citraconic acid from citraconanil is a decisive proof that the second assumption is inadmissible, and the formation of fumaric acid for the so-called maleinanil is therefore a fact that cannot be explained by Roser's hypothesis.

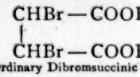
According to Anschütz, the monobrom-substitution and brom-addition-products of maleic and fumaric acids are represented by the following constitutions:



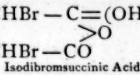
Bromfumaric Acid.



Brommaleic Acid.



Ordinary Dibromsuccinic Acid.



Isodibromsuccinic Acid.

If we accept these structural formulæ, which are a logical sequence of Roser's hypothesis, it is evident that ordinary dibromsuccinic acid on losing bromhydric acid should give bromfumaric acid, and from isodibromsuccinic acid brommaleic acid should be obtained. The experimental results of these reactions are quite the reverse, as it has been found that ordinary dibromsuccinic acid yields brommaleic acid, and isodibromsuccinic gives bromfumaric acid. It may be suggested that at least the latter of these reactions can be explained by assuming brommaleic acid to be the primary product, and that this is converted into bromfumaric acid by the bromhydric acid formed in the reaction. The conversion of brommaleic into bromfumaric acid by extremely dilute bromhydric acid has never been observed; and, moreover, even this explanation cannot be upheld, as the neutral salts of isodibromsuccinic acid also give bromfumaric acid, and the presence of free bromhydric acid under these conditions can scarcely be assumed.[1] These reactions are, in my opinion, altogether incompatible with Roser's hypothesis, and they indicate that the introconversion of maleic and fumaric derivatives is accompanied by some change in the acetylene radical. Racemic acid, according to Anschütz, contains two carboxyls, while inactive tartaric acid is a so-called dioxylactone compound. We may therefore expect that the replacement of

[1] Mesadibrompyrotartaric acid boiled with water should give, according to Anschütz, brommesaconic acid, but bromcitraconic acid is really formed in the reaction.

bromine in ordinary dibromsuccinic acid by hydroxyl should give exclusively racemic acid, but in fact a mixture of inactive tartaric and racemic acids is formed. On the other hand, isodibromsuccinic acid should yield in the same reaction inactive tartaric acid, but in reality it gives racemic acid.

Anschütz has stated his inability to explain the conversion of maleic into fumaric ether by traces of iodine, and the behavior of the first-named ether towards bromine vapor undoubtedly presents the same difficulty, although he makes no mention of this reaction in his paper. It seems almost impossible to rationally connect the conversion of maleic into fumaric ether by contact with bromine vapor, with Roser's formulæ for these compounds.

The second assumption on which Roser's constitution of maleic acid rests is that carbonyl and orthocarbonyl [$C(OH)_3$] in the γ-position are unstable, they undergoing a condensation to form an anhydride. This assumption follows from the behavior of lactones towards bases, when they take up water to form salts of oxy-acids, and the replacement of the γ-hydrogen of a lactone by negative hydroxyl can possibly have no other effect than to greatly facilitate the property of assimilating water by such compounds. It is evident that a compound like Roser's constitution of maleic acid heated with an excess of alkali must assimilate water and form a salt of mono-orthomaleic acid, but as maleic acid can be boiled with strong alkalies, and obtained unchanged by addition of mineral acids to this solution, we must, to explain this fact, assume that the free ortho-acid decomposes spontaneously into water and maleic acid. Anschütz explains the conversion of maleic into fumaric acid by mineral acids by supposing an addition and subsequent elimination of the mineral acid:

$$\begin{array}{l} CH-C(OH)(Cl)-OH \\ | \\ CH-COOH \end{array} \quad \begin{array}{l} CH-COOH \\ | \\ CH-COOH \end{array} + HCl.$$

This explanation appears to me to be in conflict with the original hypothesis. If mono-orthomaleic acid eliminates water from hydroxyls in the γ-position, the monochloride of such a compound should decompose into chlorhydric and maleic acids with still greater facility, as the replacement of one of the hydroxyls of succinic and similar acids by chlorine forms monochlorides that decompose spontaneously into anhydrides and chlorhydric acid. The

replacement therefore of a hydroxyl of mono-orthomaleic acid by the more negative chlorine could only have the effect of making the maleic character of the compound more pronounced. This contradiction becomes even more apparent in considering the conversion of maleic into fumaric acid by dilute nitric acid. Anschütz would have to explain this conversion by assuming an addition and subsequent subtraction of nitric acid in a manner similar to that already assumed with chlorhydric acid. Dilute nitric acid consists of a mixture of a strong negative compound, nitric acid, and a substance, water, that in comparison acts as a base; and it is evident that the negative anhydride of orthomaleic acid should unite with the base and not with the negative component of the mixture. If Anschütz's explanation were correct, boiling water should convert maleic much more readily into fumaric acid than dilute nitric acid does, although in fact it is without action on the acid.

The capability of compounds like Roser's maleic ether existing can hardly be doubted, and such a substance has probably been obtained by Graebe[1] by the action of tetrachlorphthalylchloride on sodium ethyl oxide, but the reactions and introconvertibility of maleic and fumaric derivatives cannot be brought in harmony with the assumption that maleic ether belongs to that group. In fact, the formation of unsymmetrical tetrachlorphthalic ether in itself contradicts Roser's views. According to his hypothesis, tetrachlorphthalic acid should have the constitution $C_6Cl_4\begin{matrix}C(OH)_2\\ \\ CO\end{matrix}>O$, and the ether obtained by the action of ethyl iodide on the silver salt of such an acid should therefore be identical with the ether obtained from the chloride and sodium ethyl oxide, while in fact two isomeric ethers were obtained. It would be no rash prediction that Graebe's unsymmetrical ether will pass over into the symmetrical form on heating, as the instability of similar unsymmetrical ethers has already been observed in ortho-compounds like $C_6H_4\begin{matrix}N(CH_3)_2\\ \\ CO\end{matrix}>O$ and $C_6H_4\begin{matrix}N(CH_3)_2\\ |\\ O\end{matrix}$, which on heating are converted into $C_6H_4\begin{matrix}N(CH_3)_2\\ COOCH_3\end{matrix}$ and $C_6H_4\begin{matrix}N(CH_3)_2\\ OCH_3\end{matrix}$; and further, that

[1] Berichte der deutsch. chem. Gesell. **16**, 860.

an acid corresponding to such unsymmetrical ethers would, if capable of existing, be extremely unstable.

In the preceding remarks, Roser's hypothesis on the constitution of maleic derivatives has been analysed for the first time, and it has been shown that while some of the reactions are incompatible with the hypothesis, others can be explained only by making a second assumption to explain the first; but a closer examination showed that these two assumptions are in themselves contradictory. These explanations are based solely on mechanical formula-twisting; a method of explaining that appeals more to the eye than to the mind, and will certainly not satisfy the present demands of organic chemistry.

TUFTS COLLEGE, MASS.

ON SULPHON-FLUORESCEIN.

BY IRA REMSEN AND C. W. HAYES.

In a brief paper[1] published some time ago, one of us (R.) gave an account of experiments which were undertaken for the purpose of studying the action of phenols upon those aromatic acids which contain carboxyl and the sulphonic acid group in the ortho position relatively to each other. It was shown that by heating resorcin and ortho-sulpho-benzoic acid together, a product is obtained which is highly fluorescent, but it was not isolated. Since the time of the publication of the paper referred to, a number of efforts have been made in this laboratory to carry the investigation to a successful issue, but one difficulty after another has been encountered. Recently we have succeeded in preparing in pure condition the first representative of the class of substances which may be called *sulphon-phthaleins*. These compounds differ from the ordinary phthaleins simply in containing the group SO_2 instead of CO. While the latter are derived from the mother substance $C\begin{cases} C_6H_5 \\ C_6H_5 \\ C_6H_4.CO \\ O\text{——}\lrcorner \end{cases}$, the sulphon-phthaleins are, in all probability, derived from a substance of the formula $C\begin{cases} C_6H_5 \\ C_6H_5 \\ C_6H_4.SO_2. \\ O\text{——}\lrcorner \end{cases}$

[1] This Journal **6**, 180.

Preparation of Sulphon-fluorescein.—As the result of a number of experiments, the following method of preparing and purifying sulphon-fluorescein was found to give the best results.

Free, dry ortho-sulpho-benzoic acid is mixed with resorcin in the proportion of 1 part acid to 1.2 parts resorcin, or a slight excess of resorcin above that required assuming that the substances act upon each other in the proportion of 1 mol. weight of the acid to 2 mol. weights of resorcin. The mixture is put in a deep vessel, a large test tube or a small beaker, which is placed in a bath of sulphuric acid, a thermometer being supported in the mixture. The bath is gradually heated. At 100° the resorcin melts and the acid slowly dissolves in the liquid. No action appears to take place until the temperature reaches 175°, when water begins to be given off and the liquid slowly becomes darker in color. White crystals of resorcin collect on the sides of the vessel. After the heating has been continued for about seven hours at 178°–185°, the liquid has a clear deep red color, but shows no signs of becoming viscous. At length lustrous, yellow, crystalline plates appear in the liquid, and soon the whole mass becomes a thick, nearly solid yellow paste. Continued heating at the same temperature apparently causes no further change. The mass, which on cooling is made up of yellow crystals imbedded in a red viscous matrix, is then dissolved in hot water, in which it forms a clear red solution, or sometimes the solution contains a very small quantity of a brown flocculent precipitate. The solution is filtered, if necessary, and evaporated to a small volume, from which on cooling the substance separates in reddish yellow radial crystals. These are filtered and washed with ether till the washings are perfectly colorless. After repeated crystallisations from water the substance has a pale straw-yellow color, and when deposited slowly, forms transparent crystal blades, sometimes attaining a length of 2.6 mm. They are arranged in radial groups.

A considerable quantity of resorcin is lost by sublimation during the reaction, especially if the operation is carried on in a beaker, so that some excess should be added. But even when the resorcin is present in excess, at the end of the reaction some free acid is always left, and this can be obtained from the mother liquors in the characteristic colorless orthorhombic crystals.

The sulphur and the water of crystallisation, or at least the water

lost by the air-dried substance when heated to 123°, were determined. In estimating the water of crystallisation, the substance was heated to 106°–123° for about ten hours till it attained a constant weight. On standing in the air it quickly regained its original weight. When heated to 130°–140° for some time it turns slightly reddish and loses over 10 per cent. of its weight, which is not regained by standing in the air.

Estimation I of sulphur was made by Liebig's method, fusing with potassium hydroxide and potassium nitrate. Estimations II and III were made by Mr. C. Mindeleff, by a method devised by Professor Morse, which will be described by him later.

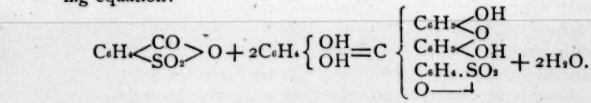
0.3882 gram heated to 106°–123° lost 0.0330 gram water = 8.5 per cent.

I. 0.2007 gram substance gave 0.1286 gram $BaSO_4$.

Estimations II and III gave 7.91 and 7.89 per cent. S respectively. The details were not furnished us, and are not at present available.

	Calculated for $C_{19}H_{12}O_6S + 2H_2O$.	Found.			
		I.	II.	III.	IV.
C	56.44	...	...	...	...
H	2.97	...	...	...	...
O	23.76	...	...	...	...
S	7.92	...	8.80	7.91	7.89
H_2O	8.91	8.5	...	...	...
	100.00				

These results show that in all probability the action of resorcin upon ortho-sulpho-benzoic acid is of the same kind as that of resorcin upon phthalic acid. Assuming that the anhydride of the acid is first formed, the reaction may be represented by the following equation:



Properties of Sulphon-fluorescein.—Sulphon-fluorescein in many respects strongly resembles v. Baeyer's fluorescein, but it also differs from it very markedly in some of its properties. In water solution it shows a weak green fluorescence, which becomes much

stronger when the solution is rendered alkaline, but it is not by any means as strong as that of fluorescein. The dilute alkaline solution appears almost perfectly colorless by transmitted light, and by reflected light a clear green. Unlike fluorescein, it is extremely soluble in water, about one part in two or three of hot, and five or six of cold water. It is also soluble in absolute alcohol, forming a yellow solution with weak fluorescence. It is soluble with difficulty in ether, but when once in solution it is deposited only on evaporating to a small volume. It does not melt at 250°, but if kept at a lower temperature for a long time it becomes red, undergoing some decomposition. If quickly heated somewhat above 300° it melts to a deep red liquid and then solidifies. If the mass is treated with water it partly dissolves, leaving a dark brown flocculent precipitate which dissolves on the addition of an alkali, the solution having an intense fluorescence, nearly, if not quite, equal to that of fluorescein. This change produced by heating has not as yet been investigated.

The crystals are very thin blades, apparently monoclinic, showing the clino-pinacoid $\infty P \infty$, and a very narrow prism ∞P and clino-dome $P \bar{\infty}$. The angle $\beta = 75°$, and the extinction angle against the c axis $= 20°$. The axial ratio could not be accurately determined.

Salts of Sulphon-fluorescein.—The influence of the group SO_3 on the chemical conduct of the compound is plainly shown by the fact that in water solution it decomposes carbonates and forms salts, which is not the case with fluorescein.

Barium salt.—Sulphon-fluorescein was boiled with an excess of carefully purified barium carbonate for two hours. The filtrate from the barium carbonate, evaporated to a small volume, deposited yellow crystals resembling the original substance, but in shorter and thicker prisms. These were twice recrystallised, and had then a light straw-yellow color. Every effort was made to secure the salt in perfectly pure condition before it was analysed, but notwithstanding this, the results obtained do not agree well with those required by the most probable formula.

I. 0.1843 gram salt gave 0.0498 gram $BaSO_4 = 15.90$ per cent. Ba.

II. 0.2620 gram salt gave 0.0708 gram $BaSO_4 = 15.89$ per cent. Ba.

Calculated for $(C_{19}H_{13}O_7S)_2Ba = 15.10$ per cent. Ba.

The water was estimated by heating at 110° until constant weight was reached. Only a part of the weight lost was regained by exposure to the air.

0.3943 gram salt lost 0.0286 gram at 110° = 7.25 per cent. water.

Calculated for $(C_{19}H_{13}O_7S)_2Ba + 4H_2O = 7.35$ per cent. water.

Although the analyses show a percentage of barium somewhat above that required by a compound of the formula $(C_{19}H_{13}O_7S)_2Ba$, still this appears to be the most probable formula for the compound. Assuming it to be correct, the first action in the formation of the salt must be the conversion of the anhydride sulphonfluorescein into the acid $C\begin{cases} C_6H_3\lessgtr^{OH}_{O} \\ C_6H_3\lessgtr^{O}_{OH} \\ C_6H_4.SO_3OH, \\ OH \end{cases}$ and the salt is derived from this acid. The results obtained agree better with the percentage of barium required by the formula $(C_{19}H_{11}O_6S)_2Ba$ which is 15.38, but the only substance from which a salt of this composition could well be formed has the constitution $C\begin{cases} C_6H_3 \\ C_6H_3\gtrless O \\ C_6H_4.SO_3OH. \\ OH \end{cases}$ Whether this is formed or not can only be determined by further experiments. By treating the salt with sulphuric acid the fluorescein is reformed.

Calcium salt.—Attempts were made to prepare the calcium salt, but without success. The sulphon-fluorescein was boiled several hours with very finely powdered Iceland spar, and some salt was formed, as shown by the evolution of carbon dioxide, but, on evaporating the solution and recrystallising the substance deposited, it was found to be the unchanged sulphon-fluorescein. There was some calcium salt in the mother liquors, but its extreme solubility prevented its separation.

Acetyl derivative of Sulphon-fluorescein.—Sulphon-fluorescein was boiled with an excess of acetic anhydride for about three hours. The solution became quite dark, and when evaporated on the water-bath it left a black tarry residue. This was treated with water, which dissolved a part, leaving a dark flocculent precipitate. The solution was boiled with bone-black and evaporated nearly to dryness. On cooling there separated a light yellow flocculent precipitate, which was very soluble in hot water and but

slightly less so in cold. This was dissolved in a small quantity of alcohol, from which it separated, on evaporation, in small radial crystals having a light lavender color and satiny lustre. They also have a peculiar odor resembling that of slippery elm, which is not removed by recrystallisation. They show a tendency to decompose, becoming yellow on exposure to the air. The substance does not melt or change in appearance under 245°. With alkalies it gives a slight greenish fluorescence. Not enough of it was obtained for the purposes of analysis. In all probability it is one of the possible acetyl derivatives of sulphon-fluorescein.

Bromine substitution-products of Sulphon-fluorescein.—When ordinary fluorescein is treated with bromine, a tetra-substitution-product is obtained most easily, and special precautions are necessary to obtain a product containing a smaller number of bromine atoms than four. With sulphon-fluorescein the case is different. It was dissolved in glacial acetic acid, in which it is soluble with some difficulty, and to the solution was added a 20 per cent. solution of bromine in acetic acid, in sufficient quantity to furnish eight atoms of bromine to one molecule of sulphon-fluorescein. This solution was evaporated on the water-bath, and, while still dilute, small, red, sharply defined crystals began to separate. The solution was evaporated to a small volume and allowed to cool, but nothing further separated. These crystals are difficultly soluble in water, alcohol, and ether. The alkaline solution shows a green fluorescence and slight red color by transmitted light. These crystals were dissolved in a large quantity of alcohol, and this solution, on evaporation, gradually deposited very small yellow crystals. These were dried in the air and analysed. The bromine was estimated by Carius' method.

I. 0.2345 gram substance gave 0.1718 gram AgBr = 31.17 per cent. Br.

II. 0.2786 gram substance gave 0.1815 gram AgBr = 27.72 per cent. Br.

Calculated for $C_{19}H_{10}Br_3O_6S$ = 30.42 per cent. Br.

These results, though unsatisfactory, indicate that, under the given conditions, it is the di-brom-sulphon-fluorescein which is formed, and not the tetra-product, as in the case of ordinary fluorescein. Whether this is due to the presence of the group SO_3 or to the difficult solubility of the di-substitution-product cannot be decided at present.

When the original acetic acid mother liquor was evaporated to dryness, a red amorphous substance remained behind which had some resemblance to eosin. The concentrated alkaline solution had a deep red color without fluorescence, and acted as a red dye. The dilute alkaline solution showed the characteristic delicate pink of eosin.

Action of concentrated sulphuric acid on Sulphon-fluorescein.—A test tube in which sulphon-fluorescein was being made broke just at the end of the reaction, and allowed the contents to run out into the sulphuric acid bath, which had a temperature of 175°. On standing several days a voluminous precipitate was deposited from the solution. This was separated by filtering through glass wool. When dry it formed a light yellow powder, extremely soluble in water, alcohol, and ether. The alkaline solution had an intense green fluorescence, with delicate shades of pink by transmitted light. On account of the extreme solubility it was found to be impossible to purify it by crystallisation. Hence the barium salt was made. The solution of the substance decomposed barium carbonate with great ease, and formed an easily soluble salt. When it was attempted to evaporate the solution of the salt to crystallisation, it was deposited in the form of a hard, insoluble, granular powder, which, on continued boiling of the solution, became brown. To avoid this the free acid was made from the barium salt by exactly precipitating the barium with sulphuric acid, and the calcium salt was then made by boiling the solution of the acid with finely powdered calcium carbonate. This also formed a hard, granular, insoluble powder on boiling, but did not change in color. As there was no guarantee of its purity and only a small quantity was obtained, it was not analysed.

Among other transformations of sulphon-fluorescein besides those already referred to, which were superficially studied, are those effected by concentrated hydrochloric acid and by reducing agents.

Concentrated hydrochloric acid does not dissolve sulphon-fluorescein, but converts it into a light yellow granular powder. When crystallised from water, in which it is quite easily soluble, it melts partially at 130°, apparently with some decomposition. The compound was not further studied.

When treated with zinc dust in a strong alkaline solution, sulphon-fluorescein is reduced to a colorless substance, probably

analogous to fluorescin. On account of its great solubility it could not be obtained in the free state. It is quickly oxidised to sulphonfluorescein by oxidising agents, as potassium permanganate and nitric acid, and passes back without further treatment if its solution be allowed to stand exposed to the air.

The investigation will be continued, and it is hoped that with a larger supply of material, some of the reactions above referred to may be cleared up.

Communication from the Chemical Institute of the University of Bonn.

CONTRIBUTIONS TO OUR KNOWLEDGE OF GLASER'S TWO MONOBROMCINNAMIC ACIDS.

BY RICHARD ANSCHÜTZ AND CHARLES C. SELDEN.

Among the isomeric monobasic acids which bear to one another relations similar to those between fumaric and maleic acids, those which offer the greatest inducement for a more thorough investigation are the two monobromcinnamic acids discovered by Glaser.[1] We have, accordingly, been engaged for a considerable time on a comparative investigation of the derivatives of these acids, supplementing the work which one of us has done on fumaric and maleic acids. In this paper an account is given of some of the results obtained by us.

The Ethers of α- and β-Bromcinnamic Acids.

Barisch[2] showed some years ago that by treating β-bromcinnamic acid with alcohol and hydrochloric acid, the ethyl ether of α-bromcinnamic acid is formed, analogous to the formation of ethers of fumaric acid from maleic acid, alcohol and hydrochloric acid. Since β-bromcinnamic acid as well as maleic acid may be changed by treatment with hydrochloric acid alone, into the other modification (the former into α-monobromcinnamic acid, the latter into fumaric acid), β-bromcinnamic acid may be compared with maleic acid as regards its action with alcohol and hydrochloric acid. If, on the other hand, instead of employing the free haloid acids for the formation of the ethers, we treat the silver salt of maleic acid

[1] Annalen der Chemie **145**, 330. [2] Journal prak. Chemie **20**, 182.

with alkyl iodides, there are in fact formed, as one of us has shown,[1] the alkyl ethers of maleic acid. We therefore treated the silver salt of β-bromcinnamic acid with alkyl iodides, a reaction which was first suggested by Barisch, and lately in the case of ethyl iodide carried out by Michael and Browne.[2]

The *methyl ether of β-bromcinnamic acid* may be made by the action of methyl iodide on the dry silver salt of β-bromcinnamic acid. It is a clear, rather oily liquid of a light yellow color. This ether, when saponified with very concentrated potash solution at a gentle heat, gave nearly pure β-bromcinnamic acid melting at 118°–119°. It distilled under diminished pressure of about 10 mm. at 145°–147° (temperature of the paraffin bath 165°–170°). By treatment with concentrated potash solution, this ether acted just as before the distillation, giving pure β-bromcinnamic acid. But if this methyl ether of β-bromcinnamic acid is heated under atmospheric pressure in a graphite bath, there distills at 286.5°–288.5° a liquid which is almost pure methyl ether of α-bromcinnamic acid, as was proved by its giving on careful saponification almost pure α-bromcinnamic acid.

Methyl ether of α-bromcinnamic acid, $C_6H_5C_2HBrO_2.CH_3$.—This ether, obtained as stated above, boils under a pressure of about 14 mm. at 158.5°–159.5° (temperature of paraffin bath 178°–183°). On analysis the following figures were obtained:

I. 0.1954 gram substance gave on combustion with lead chromate 0.3632 gram CO_2 and 0.0673 gram H_2O.

II. 0.2465 gram substance gave 0.4561 gram CO_2 and 0.0868 gram H_2O.

	Calculated for $C_{10}H_9BrO_2$.	Found. I.	II.
C	49.79	50.69	50.46
H	3.73	3.83	3.91

In both analyses the carbon was found too high, an observation of which we shall hereafter speak more definitely.

The *ethyl ether of β-bromcinnamic acid*, $C_6H_5.C_2HBrO_2C_2H_5$, is prepared from the silver salt of β-bromcinnamic acid and ethyl iodide, and is also a clear, rather thick liquid of a light yellow color. Under about 10.5 mm. pressure it boils at 151.5°–153° (temperature of the paraffin bath 175°–182°), and gives, on saponification with concentrated potash solution, pure β-bromcinnamic acid. Michael and Browne found the boiling point under 30 mm.

[1] Berichte der deutsch. chem. Gesell. **12**, 2282. [2] Ibid. **20**, 550.

pressure to be 173°–174°; we found, under about 30 mm. pressure, the boiling point 176.5°–177° (temperature of the paraffin bath 195°–202°).

I. 0.1953 gram substance gave 0.1425 gram AgBr.

II. 0.1859 gram substance gave 0.1367 gram AgBr.

III. 0.2551 gram substance gave 0.4833 gram CO_2 and 0.1042 gram H_2O.

	Calculated for $C_{11}H_{11}BrO_2$.	Found. I.	II.	III.
C	51.76	...	...	51.67
H	4.31	...	...	4.53
Br	31.38	31.05	31.29	...

The *ethyl ether of α-bromcinnamic acid*, $C_6H_5C_2HBrO_2C_2H_5$, is formed by distilling the ethyl ether of β-bromcinnamic acid under ordinary pressure, at 293.5°–295.5° in a graphite bath. This, as will be seen, is about the same temperature as is given by Barisch and by Michael and Browne for the boiling point of the ethyl ether of α-bromcinnamic acid (made by them from α-bromcinnamic acid, alcohol and hydrochloric acid). As was observed during the rectification under diminished pressure, the ethyl ether of β-bromcinnamic acid had, in the distillation under ordinary pressure, undergone, in part, a further decomposition. The ethyl ether of α-bromcinnamic acid boiling at 159°–160.5° (temperature of the paraffin bath 185°), which was obtained by fractional distillation under a pressure of 10 mm., gave on analysis the following figures:

I. 0.2632 gram substance gave 0.5080 gram CO_2 and 0.1056 gram H_2O.

II. 0.2336 gram substance gave 0.4510 gram CO_2 and 0.0927 gram H_2O.

	Calculated for $C_{11}H_{11}BrO_2$.	Found. I.	II.
C	51.76	52.63	52.65
H	4.31	4.45	4.40

For the ethyl ether of α-bromcinnamic acid obtained from α-bromcinnamic acid, alcohol and hydrochloric acid, Michael and Browne give, under 30 mm. pressure, the boiling point 202°; under about 29.5 mm. pressure we found, however, 186.5°–188.5° to be the boiling point of the ethyl ether of α-bromcinnamic acid obtained by distillation of the ethyl ether of β-bromcinnamic acid. This ether (analysis above) gave, on careful saponification with

potash solution in the cold, α-bromcinnamic acid melting at 130°–131°, which on analysis gave the following figures:

I. 0.1912 gram substance gave 0.3373 gram CO_2 and 0.0572 gram H_2O.

II. 0.1718 gram substance gave 0.3010 gram CO_2 and 0.0501 gram H_2O.

	Calculated for $C_9H_7BrO_2$.	Found. I.	Found. II.
C	47.57	48.10	47.77
H	3.08	3.33	3.24

We are in doubt whether the transformation of the alkyl ethers of β-bromcinnamic acid into the alkyl ethers of the α-bromcinnamic acid is caused by the high temperature of distillation under common pressure. Both the ethers of α-bromcinnamic acid which were obtained by distillation showed on analysis a somewhat too high percentage of carbon. The explanation of this fact may be that hydrobromic acid had split off from a small portion of the ethers of bromcinnamic acid, thus forming the corresponding ethers of phenyl propiolic acid. The haloid acid thus set free could, perhaps, play an important part in the transformation of the ethers of β-bromcinnamic acid into the corresponding ethers of α-bromcinnamic acid.

In the following table are given the boiling points, under diminished pressure, of the four ethers of bromcinnamic acid which have been investigated:

	Pressure about.	Temperature of the bath.	Boiling point.
Methyl ether of β-bromcinnamic acid	11 mm.	165–170°	145 –147°
" α- "	14	178–183	158.5–159.5
Ethyl ether of β- "	10.5	175–182	151.5–153
" α- "	10	185	159 –160.5

On comparing the α-bromcinnamic acid and β-bromcinnamic acid with fumaric acid and maleic acid, it is found that the α-acid evidently corresponds to fumaric acid and the β-acid to maleic acid. One of us has already shown [1] that the ethers of maleic acid boil at a higher temperature than the corresponding ethers of fumaric acid; we should therefore expect to find the boiling points of the ethers of the β-acid higher than those of the ethers of the α-acid. But in reality it is just the reverse.

The *chloride of α-bromcinnamic acid*, $C_6H_5C_2HBrOCl$.—Before describing this compound, which is formed by the action of phos-

[1] Berichte der deutsch. chem. Gesell. 12, 2280.

phorus pentachloride on both α- and β-bromcinnamic acid, we call attention to the results of a study of the action of phosphorus pentachloride on maleic acid which one of us made a short time ago in connection with Mr. Wirtz.[1] A compound was at that time obtained which boiled, under the same pressure, at a higher temperature than fumaryl chloride, and which gave, by analysis, figures agreeing with the formula $C_4H_3Cl_3O_2$. But this compound, although preserved in a sealed tube, underwent a change spontaneously, being apparently transformed into fumaryl chloride. The investigation of this reaction will soon be taken up again; it was temporarily interrupted because it was found necessary first to become acquainted with the anilides of fumaric and maleic acids.

Our efforts to obtain from β-bromcinnamic acid a chloride different from that of α-bromcinnamic acid have been without success. Even when using salts of β-bromcinnamic acid instead of the free acid, a compound was obtained which in all its properties was identical with the chloride of α-bromcinnamic acid.

The chloride of α-bromcinnamic acid is a clear, oily, light yellow liquid which boils, under about 12 mm. pressure, at 152°–153° (temperature of the paraffin bath 177°).

I. 0.1822 gram substance gave 0.2425 gram AgCl + AgBr and 0.0016 gram Ag.

II. 0.1670 gram substance gave 0.2213 gram AgCl + AgBr and 0.0014 gram Ag.

III. 0.2002 gram substance gave 0.3227 gram CO_2 and 0.0472 gram H_2O.

IV. 0.3197 gram substance gave 0.5173 gram CO_2 and 0.0727 gram H_2O.

	Calculated for C_9H_6BrClO.	Found. I.	II.	III.	IV.
C	43.99	...	...	43.97	44.13
H	2.44	...	...	2.62	2.52
Br + Cl	47.04	46.87	46.59	...	...

In contact with water, the chloride of α-bromcinnamic acid is very slowly transformed into α-bromcinnamic acid; with ammonia it gives the amide, and with aniline the anilide of α-bromcinnamic acid, both of which are described below. The latter compound has been of special use in identifying the chloride obtained from β-bromcinnamic acid as the chloride of α-bromcinnamic acid.

The *amide of α-bromcinnamic acid*, $C_6H_5.C_2HBrO.NH_2$, is

[1] Berichte der deutsch. chem. Gesell. **18**, 1947.

obtained by bringing together the chloride of *a*-bromcinnamic acid and an excess of aqueous ammonia. It crystallises from hot water, in which it is difficultly soluble, in the form of very thin leaves possessing a pearly lustre. Melting point 118.5°–119°.

I. 0.1651 gram substance gave 0.1371 gram AgBr.

II. 0.0839 gram substance gave 0.0690 gram AgBr.

III. 0.2649 gram substance gave 14 ccm. N at 16.5° and under 756.45 mm. pressure.

	Calculated for C_9H_8BrNO.	Found. I.	II.	III.
Br	35.40	35.33	35.00	...
N	6.19	...	...	6.10

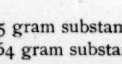
Anilide of a-bromcinnamic acid, $C_6H_5C_2HBrONH.C_6H_5$.—This compound is formed by the action of aniline on the chloride of *a*-bromcinnamic acid, a reaction by which considerable heat is evolved. It crystallises from alcohol in the form of little white needles melting at 80°. On standing for a number of days in the alcoholic mother liquor, these needles change of their own accord into six-sided plates, the melting point, however, remaining unaltered.

I. 0.1845 gram substance gave 0.1135 gram AgBr.

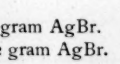
II. 0.2264 gram substance gave 0.1402 gram AgBr.

	Calculated for $C_{15}H_{12}BrNO$.	Found. I.	II.
Br	26.49	26.18	26.35

NOTE.— In the paper on "The Isomerism of Fumaric and Maleic Acids" (this Journal 9, 253) I have attempted to prove for these substances the following formulas:

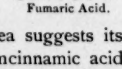


Fumaric Acid.

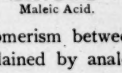


Maleic Acid.

The idea suggests itself that the isomerism between the two monobromcinnamic acids may be explained by analogous constitutional formulas, thus:



a-Bromcinnamic Acid.



β-Bromcinnamic Acid.

For the present, however, I place no special value upon these formulas, because their only support is that they make it possible to present the distant analogy with the above expressions for fumaric and maleic acids. As in the case of the last two named acids, so also in that of the α- and β-bromcinnamic acids, there is only one way to decide, that being by experimental investigation. I hope soon to be in a position to communicate the results of some researches made in the above mentioned direction.—ANSCHÜTZ.

NOTES.

Quadrivalence of Tellurium towards Chlorine.

A. Michaelis has determined the specific gravity of the vapor of tellurium tetrachloride, and has found that it corresponds to the formula $TeCl_4$, even when the vapor is heated far above the boiling point of the compound. The determinations were made at the temperature of boiling sulphur and that of boiling phosphorus pentasulphide. It is interesting to note how the stability of the tetrachlorides of the members of the sulphur group increases with the atomic weight. Sulphur tetrachloride exists only in liquid condition below 21°; selenium tetrachloride breaks down into the monochloride and chlorine when heated to boiling: $2SeCl_4 = Se_2Cl_2 + 3Cl_2$.—(*Berichte der deutschen chemischen Gesellschaft* **20,** 1780.)

On Potassium Germano-fluoride.

The fact that germanium is a member of the silicium group suggests the possibility of preparing a salt of the formula K_2GeF_6, analogous to potassium fluo-silicate, K_2SiF_6. Gerhardt Krüss and L. F. Nilson have made the salt by dissolving germanium oxide in hydrofluoric acid and adding potassium fluoride to the solution. The salt resembles the corresponding silicium salt very closely, having the composition represented by the above formula. As regards solubility it lies between the silicium salt and the corresponding tin salt; just as the position of germanium itself in the periodic system is between that of silicium and that of tin. In his paper on the periodic law which appeared in 1870,[1] Mendelejeff, in describing the properties of the then unknown eka-silicium, said: "There is no doubt that eka-silicium will yield a series of

[1] Annalen der Chemie, Sup. **8,** 201.

double fluorides (K_2EsF_6) isomorphous with the corresponding salts of silicium, titanium, zirconium, and tin. The potassium salt will be more soluble in water than the corresponding silicium salt. Eka-silicium fluoride, like titanium, zirconium, and tin fluorides, TiF_4, ZrF_4, and SnF_4, will not be a gas."—(*Berichte der deutschen chemischen Gesellschaft* **20,** 1698.)

On the Removal of Arsine from Hydrogen Sulphide.

For the purification of hydrogen sulphide made from the ordinary reagents, O. Jacobsen recommends passing the gas over some solid iodine before it is washed with water. This method is based upon the well-known facts that arsine and iodine react violently at the ordinary temperature, forming arsenic triiodide and hydriodic acid, while hydrogen sulphide does not act at all upon iodine in the solid state or disolved in strong hydriodic acid. Experiment showed that 2 to 3 grams of iodine were sufficient completely to purify a current of hydrogen sulphide made from the ordinary reagents, and running uninterruptedly for a day. The iodine is coarsely powdered, dried in the air, and then placed in a comparatively narrow glass tube, 30–40 cm. in length, a layer of glass wool being put at each end. In chemico-legal examinations, it is recommended that a second shorter tube containing some iodine be introduced, and that after the analysis this be sealed and put aside. If it can be shown that the iodine in this second tube contains no arsenic, evidence will thus be furnished that the hydrogen sulphide used was pure. It is not advisable to dry the iodine thoroughly, as the reaction is aided by the formation of a thin layer of a solution of iodine on the particles of iodine. If it is desired to purify hydrogen, this should first be passed over iodine as above described, then over glass wool which is moistened with a concentrated solution of potassium iodide, and finally washed with caustic potash.—(*Berichte der deutschen chemischen Gesellschaft* **20,** 1999.)